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FINAL REPORT

A Study of the Mechanism of the Action of Inhibitors
Which Prevent Hydrogen Embrittlement
of Carbon Steels Resulting from Acid Pickling

January 1, 1956 to November 30, 1960

Contract No. DA-30-069-ORD-1680

Placed by New York Ordnance District
For the Paint and Chemical Research Laboratory
Aberdeen Proving Ground
Aberdeen, Maryland

Contractor: The Trustees of Rutgers, The State University
in New Jersey

New Brunswick, New Jersey

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Report Prepared
by
Leonard Dauerman

Foreword

The goal of this project was to develop a general theory which would explain the mechanism of the action of inhibitors which prevent hydrogen embrittlement of carbon steels resulting from acid pickling. This work was sponsored by the Coating and Chemical Laboratory of Aberdeen Proving Ground. We are particularly grateful to two members of the sponsoring group for their substantial contributions to our work--Dr. C. Pickett, Director of the Coating and Chemical Laboratory, and Dr. M. Rosenfeld.

During the course of this work details of procedures and data were communicated through monthly and quarterly reports. These reports are available through ASTIA. This project is designated by contract number DA-30-069-ORD-1680.

A part of the material presented in this report was performed under prior contracts at Rutgers. These projects were designated by DA-30-069-ORD-1192 and DA-30-069-ORD-884.

In the course of these mechanism studies organic compounds were needed which had to be synthesized. To meet this need a separate project was sponsored by Aberdeen Proving Ground with this as its major goal. This project is designated by contract number DA-30-069-ORD-1689. The work performed by this group is presented in a separate final report.

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Summary and Conclusions

The prevention of hydrogen embrittlement of steel is an important area of investigation because of the great damage caused by this type of embrittlement. A common treatment of carbon steels is acid pickling, a process used to remove oxide film. This treatment, however, results in hydrogen embrittlement. Embrittlement caused in this way can be lessened by the addition of substances called inhibitors to the acid. An effective inhibitor in 4.8N hydrochloric acid (HCl) was found at Aberdeen Proving Ground. This was a mixture of p-toluidine and hexamine (hexamethylene tetramine). (See U. S. Army specification No. 4-105.) The decision to try this mixture was arrived at empirically since no valid theory of embrittlement inhibition was available. In the absence of such a theory it could not be ascertained whether the limits of inhibition had been reached or whether improvement was possible. Thus there were two alternatives--to continue the trial and error method or to search for a theory. The latter alternative was chosen and the problem of determining the mechanism of the action of the "Aberdeen Inhibitor" (p-toluidine and hexamine) was assigned to Rutgers as a first step in the development of a general theory of hydrogen embrittlement inhibition.

Embrittlement was measured with the Moore-Fatigue test. This may seem unusual because, more commonly, tensile and bend tests are used. The latter tests were tried first and these indicated that the "Aberdeen Inhibitor" completely prevented embrittlement; the Moore-Fatigue test showed that this was not the case. It

appears that the Moore-Fatigue test is more sensitive. Tests were made on 1095 steel. These findings were made at Aberdeen Proving Ground. [APG Reports on Project TB 4-801].

The initial problem at Rutgers was to determine whether the effectiveness of the "Aberdeen Inhibitor" was due to the substances mixed, p-toluidine and hexamine, or to reaction products. The following observations were made. In the "standard pickling solution" (4.8N HCl at 37.8°C) a reaction occurred. Several products formed and among the major ones was DHQ (3-p-tolyl-6-methyl-3,4-dihydroquinazoline). The activity of the "Aberdeen Inhibitor" could be duplicated by a mixture of 0.15% DHQ and 0.5% hexamine, and, therefore, the latter mixture was considered equivalent to the "Aberdeen Inhibitor".

The next problem was to determine the nature of the substances in solution which give rise to the inhibitory power of the mixture. Studies showed that in the acid solution DHQ is present mainly as protonated DHQ but that hexamine is solvolyzed into formaldehyde and ammonium chloride. From further studies it was concluded that the active substances in solution are DHQ and formaldehyde. These studies, however, did not exclude the possibility that a DHQ-formaldehyde interaction product is responsible for the activity of the mixture. In the acid solution these substances do not interact on mixing but it was shown that free radical conditions, UV irradiation, do produce a reaction. Since atomic hydrogen is produced during pickling, free radical conditions are also present on the surface of the metal. However, it was observed that the

effectiveness of the mixture decreases as the concentration of the interaction product increases. It was decided that the role of the interaction product, or products if formed, is negligible.

Those properties of DHQ and formaldehyde which might be related to their activity as embrittlement inhibitors were then studied. From studies of DHQ in solution the following conclusions were reached. DHQ is chemisorbed. It is adsorbed on the anodic sites on steel and, to a lesser extent, on the cathodic sites. At the 0.15% level it covers the maximum amount of the metal surface that it is geometrically capable of covering. Experiments to establish whether DHQ can catalyze hydrogen evolution, a possible way in which DHQ might act as an inhibitor, were inconclusive.

Similar studies were made using formaldehyde. Formaldehyde is adsorbed on the anodic sites and it is reduced. It appears to react with sulfur in the steel because dimethyl sulfide was detected after pickling. Since sulfur is known to accelerate hydrogen embrittlement a possible mechanism for the action of formaldehyde suggested by this observation is that it combines with sulfur. An experiment was designed to test this hypothesis; no supporting evidence was found.

Studies were made upon mixtures of DHQ and formaldehyde. From three different tests, (1) Moore-Fatigue,* (2) corrosion potential* and, (3) "diffusion potential",* it was concluded that DHQ and formaldehyde play independent roles on the metal and that the molecular size of formaldehyde is an important factor--perhaps

*These types of experiments are discussed in Section V.

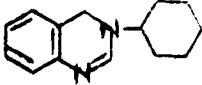
the critical factor--in determining its activity.

Several substances similar in structure to DHQ but differing in basicity were synthesized and their corrosion and embrittlement inhibition properties were studied. It was observed that in the series the substance possessing the highest pKa was the best inhibitor

From the data gathered, Dr. Rosenfeld of Aberdeen Proving Ground proposed a theory to explain the activity of DHQ and formaldehyde. It is postulated that atomic hydrogen produced on the cathodic areas of the metal during pickling enters the metal at the anodic area and that the efficiency of the inhibitor to prevent embrittlement is proportional to the fraction of the anodic area covered. A mathematical consequence is that the higher the pKa of an inhibitor, the greater the proportion of the anodic area that it blocks. Thus, if one compares a series of substances in which the hydrogen evolved is not greatly different, the substance with the highest pKa should prevent hydrogen diffusion best and therefore, should be the best hydrogen embrittlement inhibitor.

If the postulates are valid then the ratio of "Hydrogen evolved/Hydrogen diffused into metal" should be greater for inhibited than uninhibited solutions; it should also increase with the pKa of the inhibitor. Work was started on making these measurements which would test the theory but was not completed.

It also follows from this theory that a substance similar to DHQ possessing a higher pKa than any substance previously tested should be a better inhibitor than any previously tested. To meet these requirements a new substance had to be synthesized which, it was predicted, would have a pKa of approximately 8, one pKa unit

greater than any of the tested substances. This substance, 3-cyclohexyl-DHQ [] was synthesized. However, the amount synthesized prior to the termination of this project was not sufficient to be evaluated.

Several related basic studies were also made. An extensive study of the relationship between the reduction of an inhibitor and its effectiveness as an embrittlement inhibitor was made. The major conclusion was that substances which are reduced by electron absorption from the metal followed by proton absorption will cause an increase in hydrogen embrittlement; on the other hand, those substances which combine directly with atomic hydrogen should inhibit embrittlement.

A study of the data from the Moore-Fatigue test and the "diffusion potential" test, the results of which are a direct function of the amount of hydrogen diffusion into the metal, show that fatigue test differences are proportional generally to the different amounts of hydrogen which have diffused into the metal. The generally observed relationship is that the greater the decrease in fatigue strength, the greater the amount of hydrogen which diffuses into the metal.

Various ionic radicals containing as the central atoms elements from groups 5 and 6 of the periodic table were studied as corrosion inhibitors. It was observed that a free electron pair on the central atom is generally necessary for an ion to act as an effective inhibitor.

Another study was concerned with the way in which sulfur accelerates corrosion in acid solutions. Cyanide ion has been reported to accelerate corrosion by forming a complex with ferrous ion. An experiment was designed to determine whether sulfur also acts in this manner. No supporting evidence was found. Our results suggest that sulfur forms an activation complex with ferrous ion thereby lowering the activation energy necessary for iron dissolution.

A new value for the E° of iron was determined from polarization studies. To check the validity of this value which is radically different from previous ones another study using a different method, not dependent on electrochemical measurements, was begun but was not completed prior to the termination of the contract.

The experiments and the data relevant to establishing the conclusions in this section are presented in the following sections.

I.A. Extraction, fatigue testing, and "diffusion potential" testing indicate that DHQ and hexamine are the active substances in the "Aberdeen Inhibitor".

The "Aberdeen Inhibitor" consists of a mixture of p-toluidine and hexamine in the "standard pickling solution". It was found that these substances react and several products are formed. Extraction of these products was effected using common organic procedures. The major one is DHQ. A mixture of 0.15% DHQ and 0.5% hexamine was found to be equivalent to the "Aberdeen Inhibitor" as a fatigue inhibitor. These are the pertinent data from the Moore-Fatigue test.*

Table 1

<u>Treatment</u>	<u>Cycles to break (x 10⁻³**)</u>	<u>Rel. Mean Deviation</u>
"Aberdeen Inhibitor"	524	25%
0.15% DHQ and 0.5% hexamine	520	35%

The necessity for using the mixture is illustrated by the following data obtained on specimens from a different rod.

Table 2

<u>Treatment</u>	<u>Cycles to Break (x 10⁻³)</u>
0.15% DHQ and 0.5% hexamine	541
0.15% DHQ	407
0.5% hexamine	300

This finding is also supported by data from an experiment which measures hydrogen diffusion inhibition, the "diffusion

*This test is discussed in Section V.A.

**The better the inhibition, the larger the number of cycles to cause breaking.

potential" * experiments. In general, differences in fatigue inhibition are due to differences in the amount of hydrogen which the inhibitors allow to enter the metal. ** Therefore the "diffusion potential" test represents an independent check upon the fatigue test. In these experiments the longer the time-lag measured between the addition of the "standard pickling solution" and the observation of the change in the potential of the surface of the metal not in contact with the pickling solution, the better the inhibitor. These are the data obtained.

Table 3

<u>Treatment</u>	<u>Mean time-lag***</u>	<u>Standard Deviation</u>
0.15% DHQ	21.4	± 0.7
Satd. DHQ (~0.4%)	22.3	± 0.4
0.5% hexamine	9.6	± 1.5
0.15% DHQ + 0.5% hexamine	32.2	± 1.9

It is noteworthy that nearly tripling the concentration of DHQ used in the mixture in the absence of hexamine has hardly any effect, thus, the necessity for using hexamine with 0.15% DHQ is not due to an insufficient amount of DHQ in solution.

*This test is discussed in Section V.D.

**A study of the relationship between the results from the Moore-Fatigue and the "diffusion potential" experiments is presented in Section IV.B.

***The dimensions for the time-lags given for the "diffusion potential" experiment is seconds.

I.B. Hexamine in the "standard pickling solution" appears to be solvolyzed into formaldehyde and ammonium chloride.

Calculations based upon thermodynamic data reported by other investigators indicated that in the "standard pickling solution" hexamine should solvolyze into formaldehyde and ammonium chloride. This was tested by comparing the corrosion inhibition effectiveness of a solution prepared by mixing formaldehyde and ammonium chloride to one which was prepared with hexamine. No significant difference was observed. This was also the case when a solution prepared from formaldehyde was compared to one prepared from hexamine as a fatigue inhibitor. It was concluded from these results that the hexamine is not present as such in the "standard pickling solution" and that the active substance is formaldehyde.

1. Thermodynamic Calculations

The equilibrium for the solvolysis of hexamine is



The expression for the equilibrium constant is

$$(2) \quad K = \frac{[\text{CH}_2\text{O}]^6 [\text{NH}_4^+]^4}{[(\text{CH}_2)_6\text{N}_4] [\text{H}^+]^4}$$

Equilibrium constants for this reaction at several temperatures have been reported by E. Baur and W. Ruetschi.¹ The constant

(1) E. Baur and W. Ruetschi, Helv.Chim.Acta., 24, 767 (1941).

corresponding to the temperature at which our experiments are performed is 6.48×10^{10} .

$$(3) \quad 6.48 \times 10^{10} = \frac{[\text{CH}_2\text{O}]^6 [\text{NH}_4^+]^4}{[(\text{CH}_2)_6\text{N}_4] [\text{H}^+]^4}$$

The following values can be substituted into equation (3).

(3a) $[H^+] = 4.8$ It is assumed that $[H^+]$ does not change appreciably from its initial value.

(3b) $[(CH_2)_6N_4] = 0.035 - X$

where

0.035 = initial concentration

X = amount decomposed.

(3c) $[CH_2O] = 6X$

(3d) $[NH_4^+] = 4X$

Upon substituting into (3) the above values and rearranging,

(4) $X^{1.0} \times 2.86 \times 10^6 X - 1 \times 10^5 = 0.$

This equation is solved by the method of successive approximations

A perfect solution of eqn. (4) would be a value of X which renders the left hand side of the equation equal to 0. Since the maximum values of $X = 0.350$, complete decomposition, and $X = 0.0349$ is a value for which the left-hand side approaches 0, the value of X must be between 0.0349 and 0.0350. It cannot be 0.0350 because eqn. (3) would then consist of the inequality $6.48 \times 10^{1.0} = \infty$. One can say that hexamine is decomposed at least to the extent of 349 in 350 parts of 99.8% which for our purposes can be considered complete if thermodynamic equilibrium occurs.

2. Corrosion Experiments

Corrosion studies were made in which freshly prepared and three-hour-old hexamine solutions and a solution of its decomposition products, formaldehyde and ammonium chloride, were compared. Samples

were removed after a fifteen minute interval. The data are presented in Table 4.

Table 4

Corrosion Rates in "standard pickling solution" *

<u>Substance</u>	<u>Corrosion Rate After 15 min. (mg/h</u>
0.5% Hexamine (freshly prepared)	6.7
0.5% Hexamine (3 hrs. old)	6.9
0.64 % Formaldehyde** + 0.77% Ammonium Chloride	6.8

The differences obtained are considered to be within the experimental error and, therefore, are not regarded as significant.

3. Moore-Fatigue Experiments

In these experiments formaldehyde and hexamine were compared. The data are presented in Table 5. The standard deviations are approxi

Table 5 - Moore-Fatigue Experiments

<u>Treatment (in "standard pickling solution")</u>	<u>Average Cycles to failure</u>	<u>No. of Samples test</u>
0.5% Hexamine	300	4
0.64% Formaldehyde	261	4

25% and because of this relatively high standard deviation and the relatively small number of specimens tested the differences between the averages is not statistically significant.

* The method of performing the corrosion tests is described in Sections V.B. and V.C.

** Complete decomposition of hexamine will result in 6 moles of formaldehyde for each mole of hexamine which decomposes. 0.5% hexamine corresponds to 0.03M hexamine solution. Therefore, a comparable formaldehyde solution is 0.216 M or 0.64%.

I.C. The DHQ-hexamine interaction product and its significance.

The possibility that DHQ and formaldehyde react to form a product which is the source of the inhibiting power of the mixture was studied. Under normal conditions such a reaction does not occur. But free radical conditions prevail on the surface of steel during pickling because atomic hydrogen is produced. A question arose as to whether such conditions could effect a reaction. No attempt was made to isolate a possible interaction product directly from a pickling solution following metal attack because it was believed that the amount formed would be too small to isolate without great difficulty. To test the possibility that free radical conditions can bring about a reaction, a mixture of DHQ and hexamine in the "standard pickling solution" were irradiated with ultraviolet light. UV irradiation effected a reaction. As the amount of this product in solution increased, the corrosion inhibition properties of the solution decreased. It was therefore concluded that if such a product did form during pickling it would not play a significant role as an inhibitor. Details of the experiments performed are presented below.

Two solutions of 0.15% DHQ and 0.5% hexamine in 4.8 N hydrochloric acid were exposed to sunlight, a simple source of UV. The heating effect was not considered important because it had been shown that heat alone does not bring about a reaction. The first solution (R-I) was exposed in the presence of air, while the second (R-II) was kept under nitrogen.

The solutions were tested in two different ways. The first was the isolation of the products and the second was the determination of the corrosion inhibition effectiveness of the mixtures.

1. Isolation of the products

As a "blank" a fresh solution of DHQ and hexamine in 4.8 NHCl was made alkaline. A white crystalline material was obtained, the amount of which was equivalent to the amount of DHQ originally added. In addition the UV spectrum contained the characteristic DHQ peaks (228 mμ and 313 mμ) and an IR spectrum identical to that of DHQ. The R-I and R-II solutions were treated in a similar manner. Following exposure^{R-I} was made alkaline and a brown material was obtained. This material did not absorb in the ultraviolet. It did absorb in the visible region but no definite peak was observed. The infrared spectrum of this material did not agree with that of DHQ. The amount obtained was twice the amount that could be expected if the product were DHQ. Clearly these results indicate that the DHQ has been destroyed and a new substance or substances have been produced. Because of the large weight increase it appears that the DHQ must have been combined with the formaldehyde or some derivative thereof.

Similar treatment of R-II resulted in a very small amount of a brown substance which had UV absorption peaks at 305 mμ and 437 mμ, significantly different from those of DHQ. The infrared spectrum of this material was similar but not identical to that of DHQ.

2. Corrosion Inhibition

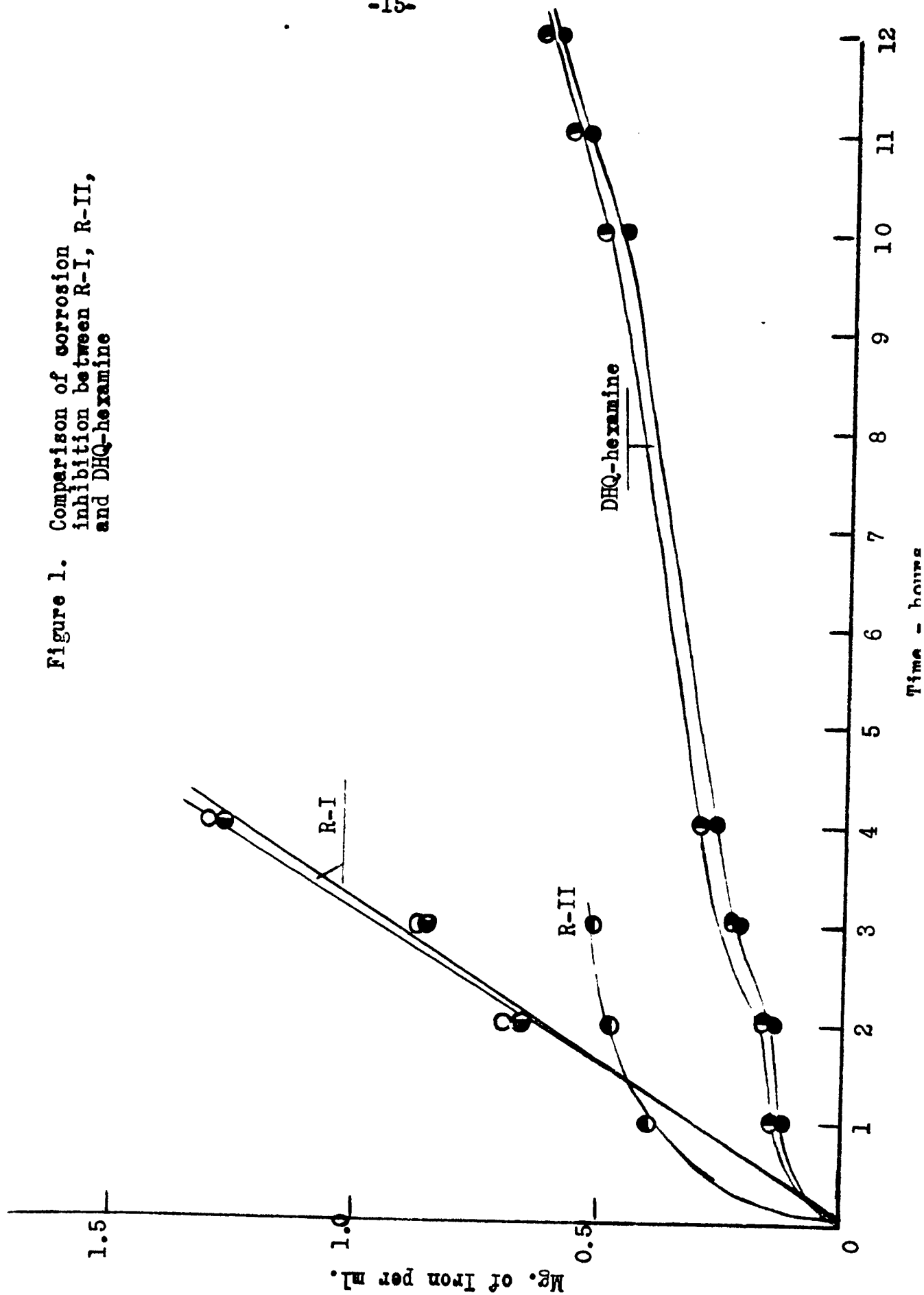
The corrosion inhibiting powers of R-I and R-II were compared to that of a freshly prepared DHQ-hexamine solution. The data are presented in Table 6 and plotted in Figure 1. It was found that R-I and R-II are inferior to the freshly prepared DHQ-hexamine solution. It appears then that the effective corrosion inhibition is due to DHQ and hexamine and not some interaction product.

Table 6

Relative Corrosion Rates of Mixtures Studied

<u>R-I</u>		<u>R-II</u>		<u>DHQ-Hexamine</u>	
<u>Time(Hrs.)</u>	<u>Fe/ml.,mg.</u>	<u>Time(Hrs.)</u>	<u>Fe/ml.,mg.</u>	<u>Time(Hrs.)</u>	<u>Fe/ml.,mg.</u>
2	.695	1	.400	1	0.12
2	.663	2	.475	1	0.15
3	.855	3	.510	2	0.14
3	.865			2	0.16
4	1.27			3	0.21
4	1.30			3	0.22
				4	0.265
				4	0.30
				10	0.46
				10	0.50
				11	0.54
				11	0.58
				12	0.595
				12	0.635

Figure 1. Comparison of corrosion inhibition between R-I, R-II, and DHQ-hexamine



II.A. Properties of DHQ observed.

1. DHQ is adsorbed.

This was demonstrated easily by UV analysis of isooctane extracts from a solution of 0.15% DHQ in the "standard pickling solution" before and after the addition of powdered iron. The addition of powdered iron resulted in the disappearance of the characteristic DHQ absorption band. Since it is shown in the next section and also in the hydrogen evolution studies* that DHQ is not reduced during pickling it seems reasonable to conclude that it is adsorbed.

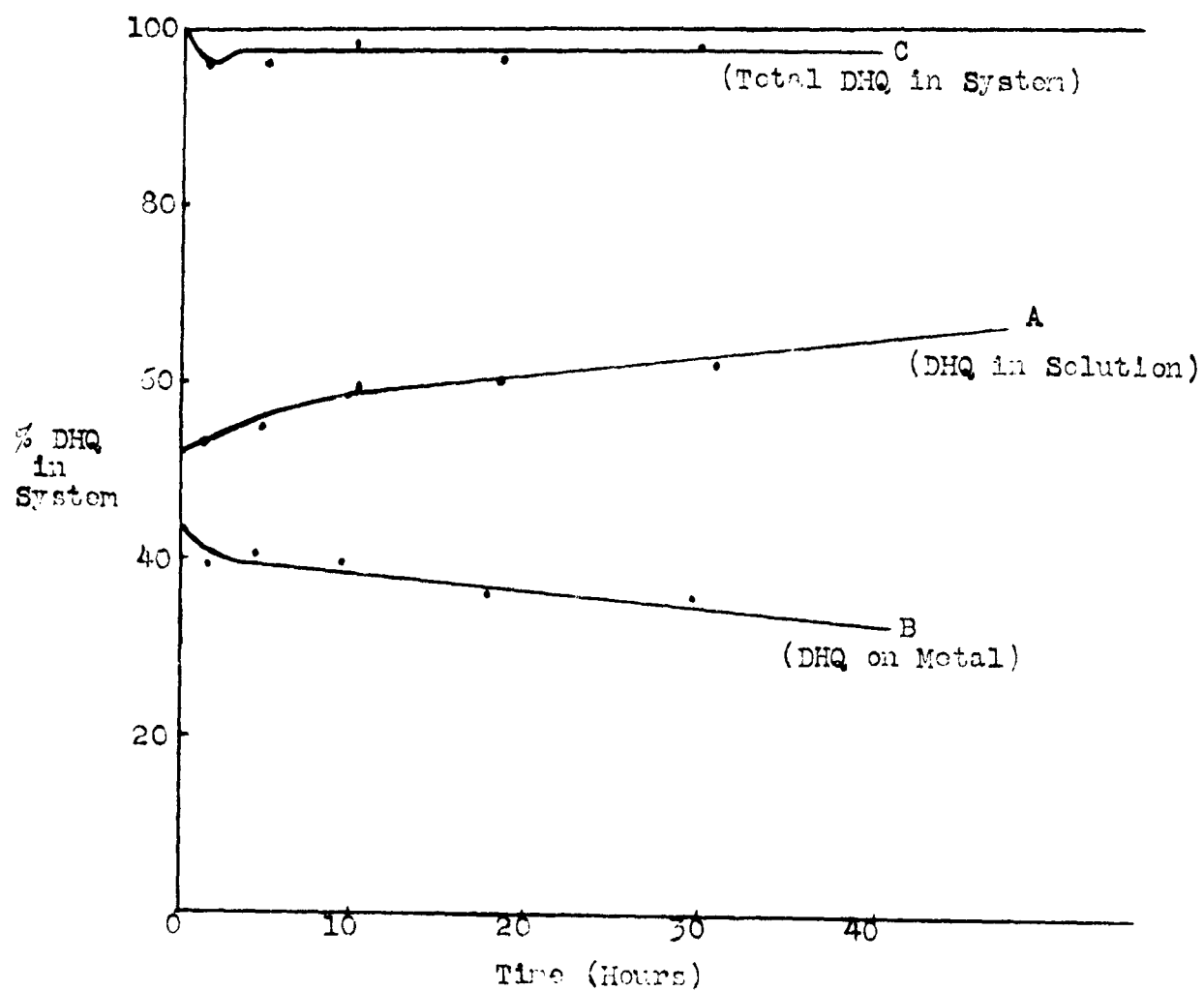
2. DHQ is not reduced during pickling.

If reduction takes place, the total amount of DHQ in the system, the sum of the amount in solution and that adsorbed on the metal, should be less than the original amount and should decrease with time. Such measurements were made. It was observed that the amount of DHQ was less than the added amount but this difference was considered within the experimental limitations of measuring the amount of DHQ adsorbed on the metal. Of greater importance, this value remained nearly constant with time which would not be the case if reduction took place. In addition, as was mentioned in the previous section, in another independent study, "hydrogen evolution studies", evidence was also found which indicated that DHQ is not reduced. The analytical procedure is presented below and the data are plotted in figure 2.

Procedure for the Analysis of DHQ in Pickling Mixtures. - A solution of 0.500 g. of DHQ in 1 liter 4.8 N HCl at 25°C. was run into a flask

* See Section IV.A.1.

Figure 2. Distribution of DHQ in System during Pickling



containing 300 g. powdered "Iron by Hydrogen". This mixture was stirred rapidly in a 25° bath while N₂ was used to exclude air. Ten ml. samples were withdrawn from time to time using a pipette fitted with a glass wool filter to exclude powdered iron.

The samples were extracted each with five 10 ml. portions of CHCl₃. The extracts were run into a flask containing small pieces of dry ice. When all of the extracts were combined anhydrous MgSO₄ was added to take up the water, the flask swirled several times, and another piece of dry ice was added. The flask was stoppered loosely while CO₂ continued to escape. Then the stopper was fixed tightly and the mixture allowed to stand for 30 min. (not more than 2 hours) To determine the amount of DHQ adsorbed on the powdered iron the above method of analysis was used on the solutions obtained by desorption with organic solvents--benzene, chloroform, and ethyl alcohol.

3. DHQ is adsorbed on both anodic and cathodic sites but predominantly on anodic ones.

A corrosion potential is defined as the measured potential of a metal undergoing corrosion referred to a standard hydrogen electrode. Such data obtained when inhibitors are present have been interpreted by T.P. Hoar^s in such a way that it is possible to tell

(2) T. P. Hoar, "Pittsburgh International Conference on Surface Reactions" p. 127 (1948).

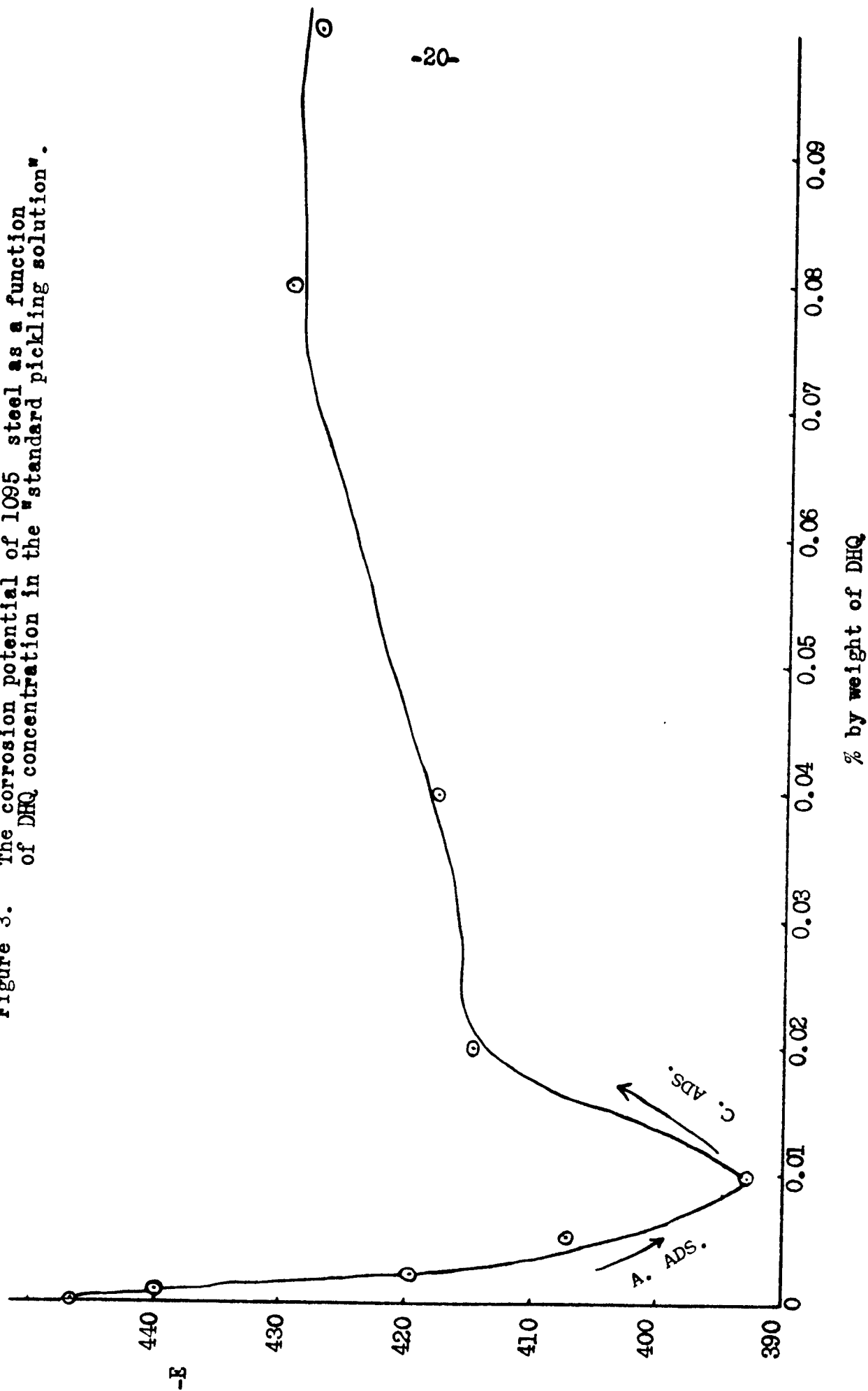
whether the inhibitor is adsorbed upon the cathodic or anodic sites on a metal, or both. The data shown in Table 7 are plotted in Figure 3.

Table 7

Potentials of 1095 steel rods in 4.8 N HCl at 37.8°C.
inhibited by DHQ compared with a S.C.E. in sat. KCl.

<u>% DHQ</u>	<u>EMF</u>
0	-448
0.001	-442
0.002	-420
0.005	-410
0.01	-396
0.02	-418
0.04	-422
0.08	-436
0.10	-438

Figure 3. The corrosion potential of 1095 steel as a function of DHQ concentration in the "standard pickling solution".



According to Hoar's explanation the increase in potential in the concentration range up to 0.01% means that the inhibitor is being adsorbed on the anode. The subsequent change in slope means that as the concentration of DHQ is increased beyond 0.01%, adsorption takes place on the cathode. In conclusion, DHQ acts primarily as an anodic inhibitor but as its concentration in solution increases it also acts as a cathodic inhibitor.

4. Chemisorption of DHQ.

Dr. Rosenfeld calculated the heat of adsorption, from the vapor state to the metal, of DHQ to be approximately 33.4 Kcal/mole. A heat of adsorption of such magnitude is indicative of chemisorption. From this value it was possible to calculate the expected heat of adsorption and temperature change when DHQ is added to a mixture of isooctane and iron powder from the following information and assumption 50 grams of 8 micron average diameter iron powder has a total surface area of $4.8 \times 10^4 \text{ cm}^2$. The heat released will be 0.26 cal.; the calculated expected rise in temperature is 0.01 degree when one takes into account the heat capacity of the iron and the calorimeter. The actual temperature increase found was 0.004 degrees. This is a significant change as shown by the fact that a Beckmann thermometer was used and because several controls were run in which no temperature rise was observed. It is lower than the expected rise but not to an unreasonable extent considering the assumptions needed to predict the temperature rise. Moreover, the adsorption took place from solution at a solid-liquid interface. The heat of adsorption corresponding to this temperature change is approximately 13 Kcal/mole, a value which is still indicative of chemisorption.

5. Solubility and the Effectiveness of DHQ.

A 0.15% DHQ solution is not saturated--such a solution is approximately 0.4%. Comparison of a 0.15% solution to a saturated one leads to an insight into the effect of relative saturation. The following data were obtained in the "diffusion potential" experiment.

Table 8

<u>Treatment</u>	<u>Mean time-lag</u>	<u>Standard deviation</u>
0.15% DHQ	21.1	± 0.7
Sat'd. DHQ	22.3	± 0.4

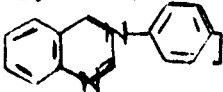
The effect is negligibly small. A more striking illustration is presented when 0.15% 3- ϕ -3,4-DHQ [] is compared to saturated 3- ϕ -3,4-DHQ. 3- ϕ -3,4-DHQ has a structure similar to that of DHQ and similar inhibiting properties. (See Section II.F.) The only sharp difference in behavior that has been observed is solubility--saturated 3- ϕ -3,4-DHQ is a 9% solution. Therefore the change in relative saturation is very great. The following data have been obtained.

Table 9

<u>Treatment</u>	<u>Mean time-lag</u>	<u>Standard Deviation</u>
0.15% 3- ϕ -3,4-DHQ	16.1	± 1.3
Sat. 3- ϕ -3,4-DHQ	20.5	± 0.8

This is a relatively small change.

It would appear from these results that at the 0.15% concentration the surface coverage ability by these inhibitors is close to the maximum.

6. Study of the Possibility that DHQ Catalyzes Hydrogen Evolution.

The Apparatus. - The apparatus used in the polarization studies with a platinum cathode is shown in Figure 4. It consists of a glass cell with provision for introducing a stream of nitrogen at the bottom of the cell. Inserted in the cell, through a rubber stopper is a conductor to a platinum sheet electrode, 10 cm. x 5 cm., a tube leading to a saturated calomel half-cell, and a siphon tube leading to a small flask in which is inserted a graphite rod to serve as the anode. The cell holds about 300 ml. of solution.

The electrical circuit is shown in Figure 5. With the double-throw switch in one position, a current from battery B polarizes the platinum electrode. The current is regulated by means of resistance R. While the current is flowing the condenser takes a charge corresponding to the potential difference existing between the platinum electrode and the calomel half-cell. When the double-throw switch is reversed, the polarizing circuit is broken and the condenser is discharged through the sensitive galvanometer G. A deflection of 10 cm. corresponds to 200 millivolts.

Procedure. - The cell is set up as described and the solution introduced. Nitrogen gas is bubbled through the solution for 20 minutes, and a polarizing current of about 2.4 milliamperes is allowed to flow for 20 minutes. A reading of the galvanometer deflection is taken, and then the charging circuit is broken and galvanometer readings are taken at convenient intervals. During the entire operation the stream of nitrogen is maintained as nearly as possible at a constant rate.

The solutions of electrolyte used experimentally in the cell were as follows.

- (1) Hydrochloric Acid 4.8 N.
- (2) Hydrochloric Acid 4.8 N + 0.15% DHQ.
- (3) Hydrochloric Acid 4.8 N + 0.15% DHQ + 0.5% Hexamine.
- (4) Hydrochloric Acid 4.8 N + 0.5% Hexamine.
- (5) Hydrochloric Acid 4.8 N + 0.5% Na_2S .

Results. - The results are shown graphically in Figure 6, in which galvanometer deflections are plotted against time in hours as abscissa.

Immediately after the polarizing current is stopped, the potential between the saturated calomel half-cell and the platinum electrode drops, corresponding to a deflection of the galvanometer of 20-24 cm. to about 7 cm. This drop takes place within one or two minutes. Thereafter the potential changes very slowly. The behavior with hydrochloric acid alone is strikingly different from that with hydrochloric acid containing DHQ and the hydrolysis products of hexamine.

- (1) Hydrochloric acid 4.8 N.

After the initial drop, the potential falls very slowly for about 3-1/2 hours, and then falls more rapidly.

- (2) Hydrochloric acid 4.8 N containing 0.15% DHQ.

After the initial drop, the potential continues to fall steadily.

- (3) Hydrochloric acid 4.8 N containing 0.15% DHQ and 0.5% Hexamine (Products of its hydrolysis).

After the initial drop the potential remains nearly constant, or at most drops very slowly. Even after 7 hours the potential has not fallen as it did in the case of hydrochloric acid above or hydrochloric acid with added DHQ.

(4) Hydrochloric acid 4.8 N containing the hydrolysis products of 0.5% hexamine.

The course of the curve is practically identical with that of (3). To avoid confusion a separate curve has not been drawn.

(5) Similar to (2) but decline is steeper.

Discussion. - We shall assume that the polarization charges the platinum electrode with hydrogen and that, as soon as the polarizing current is interrupted the hydrogen begins to be removed by solution in the acid, aided by the stream of nitrogen passing through the solution. At first the loss of hydrogen from the surface may be the rate determining process, and, in the case of the 4.8 N HCl this process is rate determining for about 3-1/2 hours. Then the diffusion of the hydrogen to the surface of the platinum is no longer able to keep the surface saturated for the particular process of removal and the potential drops more rapidly.

With the solution containing DHQ the removal of hydrogen is much more rapid, and even in the first hour a considerable drop in potential occurs.

Surprisingly, in the solutions to which hexamine was added both with and without DHQ, the removal of the hydrogen is much slower. Even after 7 hours, the drop in potential is small.

If our interpretation is essentially correct, it appears that DHQ aids in the removal of hydrogen, but that the hydrolysis products of hexamine (presumably formaldehyde) interfere with the passage of hydrogen across the interface between metal and solution. Such an inhibiting process can, of course, work both ways. It can, conceivably

prevent escape of hydrogen but it can also prevent entry of hydrogen.

The reason for testing sulfur was to test the way in which the data have been interpreted. Sulfur is a hydrogen diffusion accelerator (on steel) and, therefore, would not be expected to act like a catalyst of hydrogen evolution. But the obtained data interpreted as previously indicates that the sulfide ion is a better catalyst of hydrogen evolution than DHQ! Obviously--at least this was the thought at the time of this finding--the interpretation of the data is incorrect. In a subsequent, independent study (Section IV.C.) it was shown that while sulfur is a corrosion accelerator on steel it does not behave in an analogous manner on platinum. It also might not be a hydrogen accelerator as had been assumed. Thus the original interpretation of the data might be correct. But even if it can be shown that DHQ is a catalyst for hydrogen evolution on platinum considering the experience with sulfur we would not be certain what its behavior on steel is. This study shows that one can not substitute platinum for steel and expect, a priori, to obtain conclusions applicable to steel.

Figure 4. Hydrogen Polarization Apparatus

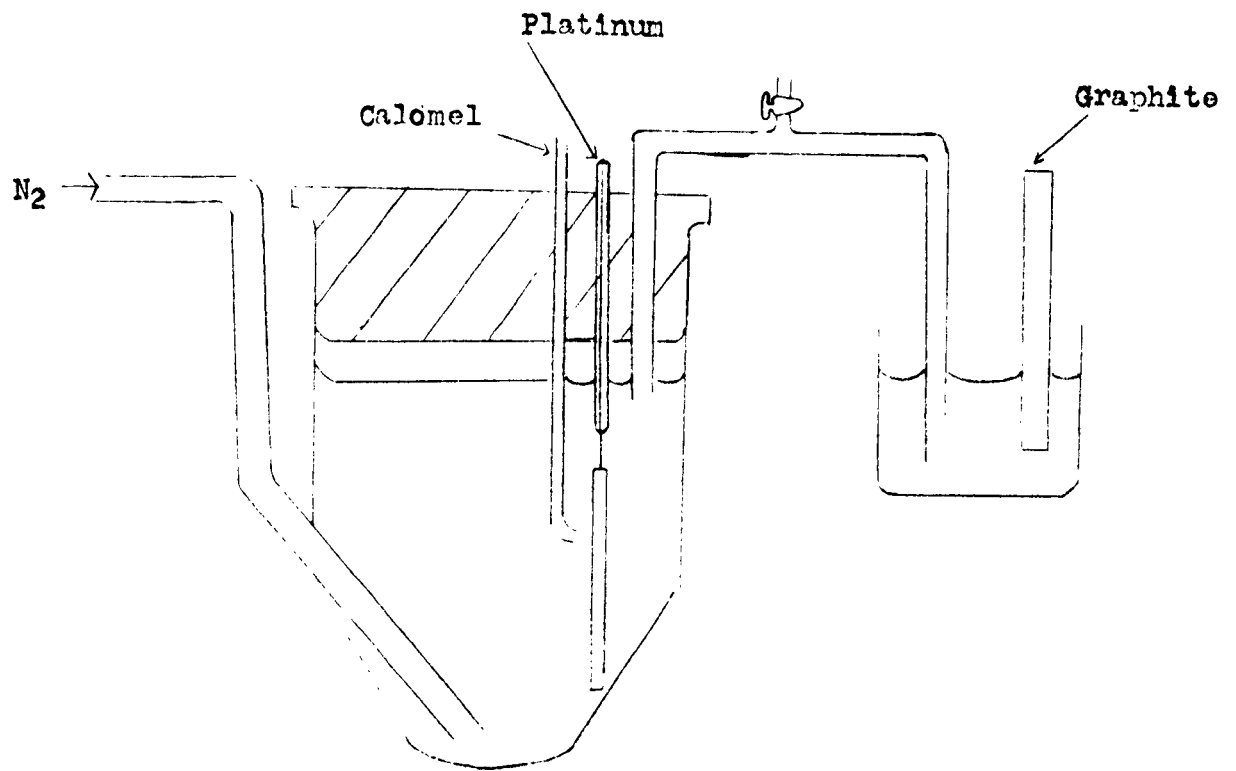


Figure 5

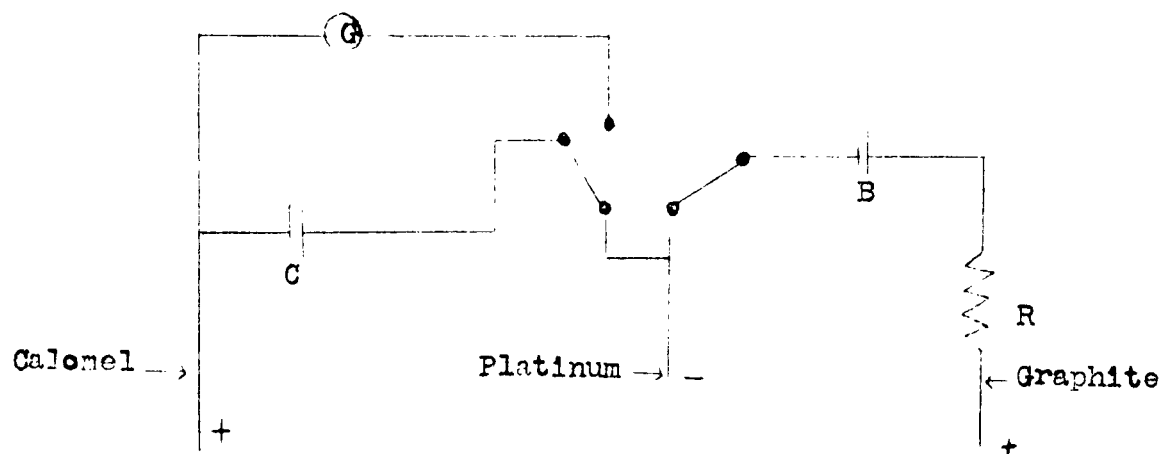
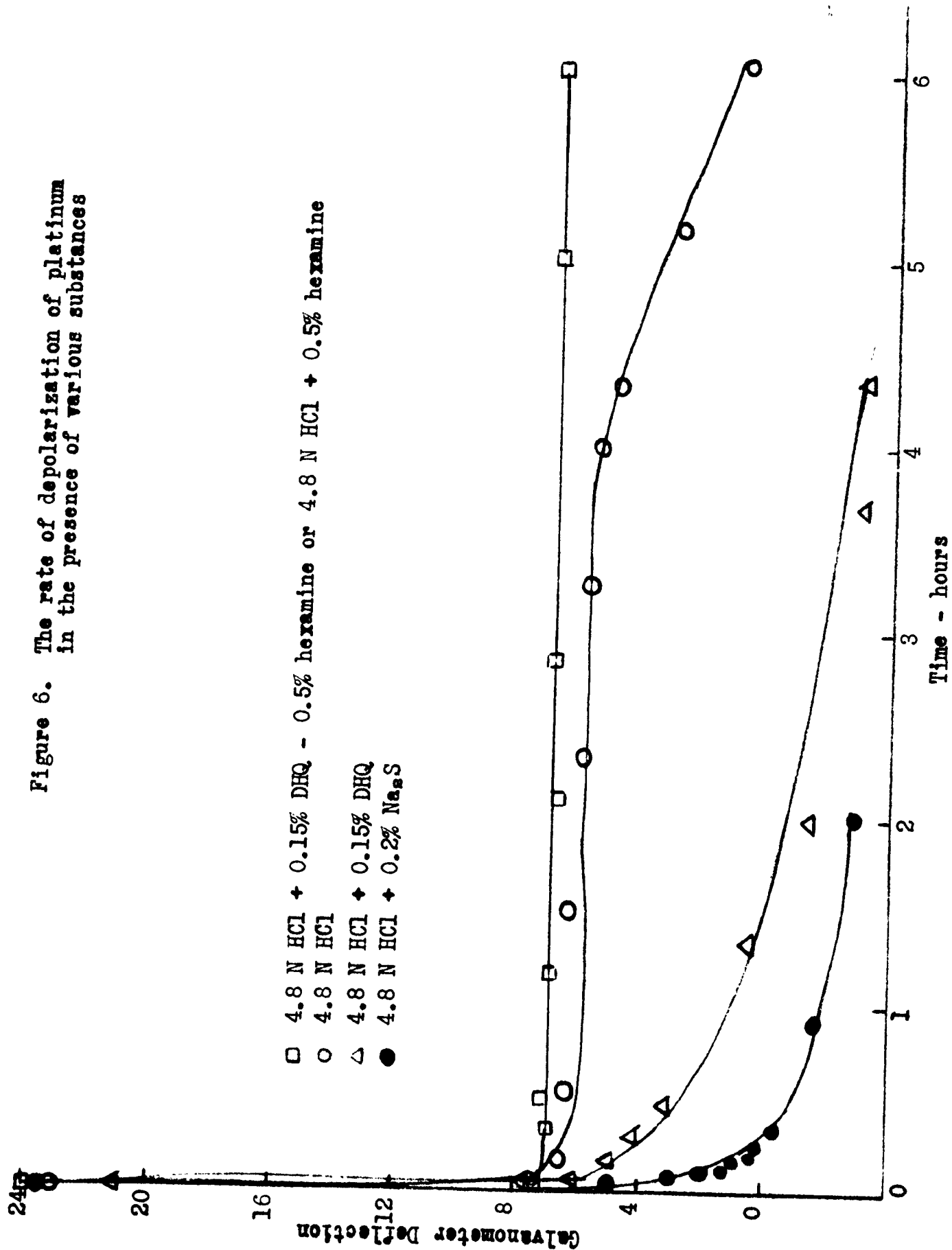


Figure 6. The rate of depolarization of platinum in the presence of various substances



II.B. Properties of Formaldehyde Observed.

1. Reduction of Formaldehyde by Iron.

A quantity of powdered iron was treated with a methanol-free solution of formaldehyde in 4.8 N HCl. After the metal had dissolved the mixture was distilled almost to dryness. This distillate was treated with aqueous ammonia to convert the formaldehyde to hexamine and again distilled almost to dryness. The liquid obtained was made slightly acid with HCl and fractionated to remove the low-boiling portion. To determine whether this low-boiling portion was methanol the preparation of a derivative was tried. This distillate was made slightly basic and treated at -15°C . with p-nitrobenzoyl chloride. The crude product so obtained was recrystallized several times and the melting point of a mixture with an authentic sample of methyl-p-nitrobenzoate was taken. No depression was observed, which means that a derivative of methanol was made and, therefore, methanol did form.

2. Combination with sulfur.

In the previously cited experiment in which the reduction of formaldehyde was observed a small amount of dimethyl sulfide was isolated. The only source of sulfur appears to have been the metal. Since sulfur on the surface of steel accelerates hydrogen embrittlement

(3) Baukloh, W., and Retzlaff, W. Arch.Eisenhüttenw 11, 97-99 (1937)

the combination of formaldehyde with it is a significant observation because it points to a possible mechanism of inhibition. In a later section this possibility was tested and it was concluded that this was

not the case, at least within the limits of the design of the test. See Section II.E.

3. Adsorption of hexamine.

The corrosion potential of 1095 steel was observed to shift in the cathodic direction from -0.482 to -0.442 volts in the presence of 0.5% hexamine. This cathodic shift signifies that adsorption is occurring predominantly on the anodic sites on the metal.

II.C. Evidence for DHQ and formaldehyde playing independent roles in inhibition.

In three major different types of tests, it was observed that the properties of a mixture of DHQ and hexamine are equal to the sum of the properties of the components tested individually. Taken collectively, these results suggest that DHQ and hexamine act independently of each other and supplement each other.

1. Adsorption of DHQ and Hexamine.

The change in the corrosion potential of 1095 steel in the standard pickling solution containing 0.15% DHQ and 0.5% hexamine is 0.1 volts. Singly, 0.15% DHQ causes a potential lowering of 0.06 volts and 0.5% hexamine, 0.04 volts. Thus the effect of the mixture is equal to the sum of the potential lowerings which occur individually. A possible explanation is that DHQ and hexamine are adsorbed independently. This is only speculative because the relationship between the corrosion potential and adsorption has not been studied.

2. Moore-Fatigue data on a mixture of DHQ and hexamine.

The following data show that the effectiveness of the mixture is approximately equal to the sum of this inhibiting powers of the components taken alone.

Table 10

<u>Treatment</u>	<u>M F_{ref} *</u>	<u>σ M F *</u>
0.5% Hexamine	0.51	0.66
0.15% DHQ	0.41	0.45
0.15% DHQ - 0.5% Hexamine	1.0	0.48

3. Diffusion Potential.

The following data show the "supplementary effect" in the diffusion potential experiments.

Table 11

<u>Treatment</u>	<u>Mean Time-lag</u>	<u>Standard Deviation</u>
0.15% DHQ	21.4	± 0.7
0.5% Hexamine	9.6	± 1.5
0.15% DHQ - 0.5% Hexamine	32.2	± 1.9

II.D. Evidence that the molecular size of formaldehyde is important.

There is further evidence for believing that hexamine plays a role independent of DHQ. This evidence comes from diffusion potential experiments in which saturated DHQ was studied and the activity of molecules approximately the same size as DHQ were studied

* The derivation of these terms are discussed in Section II.F.

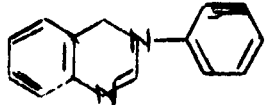
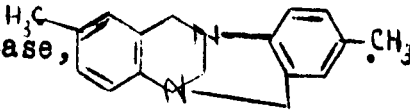
in conjunction with hexamine. There were 3- ϕ -3,4-DHQ, , and Troeger's Base, . The data are presented in the following table.

Table 12

<u>Treatment</u>	<u>Mean time-lag</u>	<u>Standard Deviation</u>
0.15% DHQ	21.4	± 0.7
Sat'd. DHQ (0.4%)	22.3	± 0.9
0.15% DHQ -0.5% hexamine	32.2	± 1.9
Sat'd. DHQ -0.5% hexamine	33.6	± 5.2
0.15% 3- ϕ -3,4-DHQ	16.1	± 1.3
Sat'd. 3- ϕ -3,4-DHQ (9%)	20.5	± 0.8
0.15% 3- ϕ -3,4-DHQ -0.5% hexamine	34.3	± 2.2
0.15% Troeger's Base	11.2	± 2.1
Sat'd. Troeger's Base	16.6	
0.15% Troeger's Base -0.5% hexamine	32.	

It is noteworthy that changing the concentration of the large molecule alone, even radically as in the case of 3- ϕ -3,4-DHQ, does not change the mean time-lag very much. But a sharp increase does occur in the presence of 0.5% hexamine. What is even more striking, the levels reached for these three different mixtures is the same within the experimental error.

These results lead to a reasonable working hypothesis for the role of hexamine. The data obtained for the large molecular-type substances in the absence of hexamine can be interpreted as meaning

that at the 0.15% concentration level these substances pack the metal surface as best they can. But because of steric factors this is imperfect. The sizes of many of the gaps can be filled by a small molecule like formaldehyde and that this is its role. If the hypothesis is correct then the effectiveness of mixtures of DHQ and aldehydes of a homologous series should decrease as the size of the aldehyde increases. This hypothesis could not be tested before the contract was terminated.

II.E. Formaldehyde does not neutralize the embrittlement accelerating properties of sulfur.

It has previously been mentioned that dimethyl sulfide had been detected, following pickling, in an analysis of a pickling solution containing formaldehyde. This was considered a significant observation because the source of the sulfur was probably the steel where it is known to act as an embrittlement accelerator. Therefore, its removal by formaldehyde should decrease embrittlement. This hypothesis was tested in the manner to be described. The test indicated that the removal of sulfur in this way probably does not affect embrittlement.

1. The effect of sulfur on hydrogen diffusion.

The following "diffusion potential" data were obtained when various amounts of sodium sulfide were dissolved in the standard pickling solution. (next page)

Table 13

<u>Concentration of $S^{=}$ (based upon addition of Na_2S)</u>	<u>Time-lag of $S^{=}$ (min.)</u>	<u>Time-lag of blank (min.)</u>
1×10^{-6} M	11.0	13.2
1×10^{-5} M	7.5	10.2
1×10^{-3} M	6.8	11.3
1×10^{-2} M	6.7	11.3
1×10^{-1} M	3.2	10.4

Thus, very small concentrations of $S^{=}$ cause significant decreases in the time-lag, which means that the hydrogen penetrates the metal at a greater rate. This effect seems to depend logarithmically on the concentration of $S^{=}$.

2. The effect of Hexamine on Sulfide Ion in Solution.

The effect of $S^{=}$ on the diffusion potential was shown in the previous experiment. It was postulated that if CH_3O is a $S^{=}$ scavenger then if present in relatively massive amounts it should neutralize the $S^{=}$. The results are shown in the following table.

Table 14

<u>Experiment No.</u>	<u>10% Hexamine in 4.8 N HCl-10^{-5} M Sulfur</u>	<u>10% Hexamine in 4.8 N HCl</u>
1	39.0	56.9
2	43.6	45.8
3	57.0	80.4

It appears that hexamine has no specific effect upon sulfur because in all of the experiments, the presence of sulfur lowered

the time-lag. In two of the experiments the time-lag is lowered by approximately 25% which is almost the same effect the presence of an equal concentration of sulfur has on uninhibited acid (see Table 13).

II.F. Comparison of the properties of several substances similar to DHQ indicate that basicity is an important factor in determining inhibition properties.

The role of the basicity of DHQ in determining its inhibitive properties was studied by synthesizing a series of substances similar to DHQ. In all of these substances the amidine-linkage, $-N-C=N-$, was retained since it was believed to confer on DHQ its special properties. The compounds synthesized differed in basicity. Other differences were also present but they were believed to play a negligible role compared to the effect of the basicity differences.

The corrosion and pickling fatigue properties of the substances with 0.5% hexamine were studied. The data obtained are shown in Table 15. The data have been plotted in Figures 7, 8, and 9.

The data in the table have been "normalized" by referring all the values to comparable values obtained for 0.15% DHQ and 0.5% hexamine on the same rod. The main purpose of this procedure is to minimize differences based upon variations inherent in the various rods. The normalized terms are obtained by the following operations.

$$1. \quad M F_{ref} = \frac{B_x - B_0}{B_{ref} - B_0}$$

where - B_x = average breaking point after pickling in acid inhibited with substance under investigation

B_o = average breaking point after pickling in uninhibited acid

B_{ref} = average breaking point of the reference mixture

2. σ M F

Standard deviation about the $M F_{ref}$ value

3. C_{ref}

$C = \frac{L_s}{L_{ref}}$ where L_s = rate of corrosion in presence of substance under investigation

L_{ref} = rate of corrosion in presence of 0.15% DHQ and 0.5% hexamine

4. $C\sigma$

Standard deviation about the C_{ref} value

Table 15

Structural Formulas of Substances Discussed in this Section

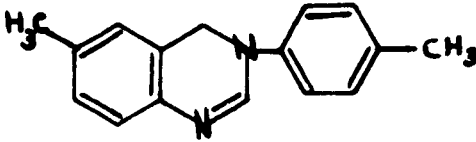
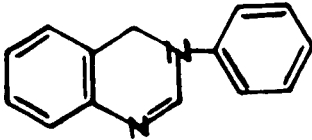
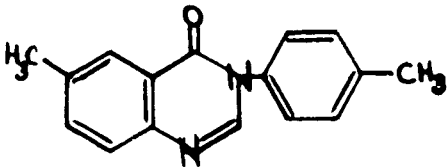
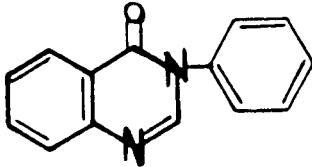
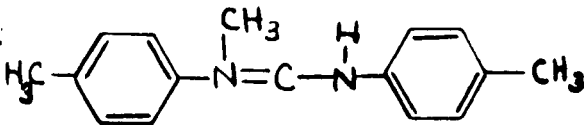
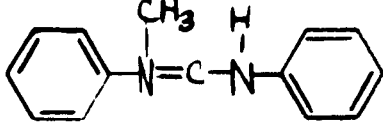
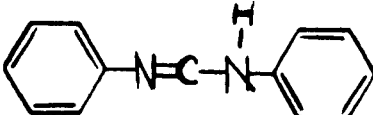
<u>Name</u>	<u>Structure</u>
1) DHQ	
2) 3- ϕ -3,4-DHQ	
3) 3-p-tolyl-6-methyl-quinazalone-4	
4) 3- ϕ -quinazalone-4	
5) N,N'-di-p-tolyl-N-methyl-formamidine	
6) N,N'-di-phenyl-N-methyl-formamidine	
7) N,N'-di-phenyl-formamidine	

Table 16

<u>Treatment</u> * *	<u>Graph Designation</u>	<u>pKa</u>	<u>M F data</u> *		<u>Corrosion data</u> *	
			<u>M F_{ref}</u>	<u>σ M F</u>	<u>C_{ref}</u>	<u>Cσ</u>
0.16% DHQ	A	6.6	1.0	-	1.0	-
0.13% 3- o -3,4-DHQ	B	6.9	1.1	-	1.8	0.78
0.16% 3-p-tolyl-6-methyl-quinazolone-4	C	2.6	0.40	2.6	10.2	6.8
0.14% 3-phenyl-quinazolone-4	D	2.7	0.25	0.025	23.4	10.2
0.15% N,N'-di-p-tolyl-N-methyl-formamidine	E	6.3	0.61	1.16	2.7	-
0.13% N,N'-di-phenyl-N-methyl-formamidine	F	-	0.74	0.18	4.4	6.4
0.12% N,N'-di-phenyl-formamidine	G	5.8	0.54	14.8	4.8	0.25

* With 0.5% hexamine present

* * Concentrations of substances tested are approximately equivalent on a molar basis.

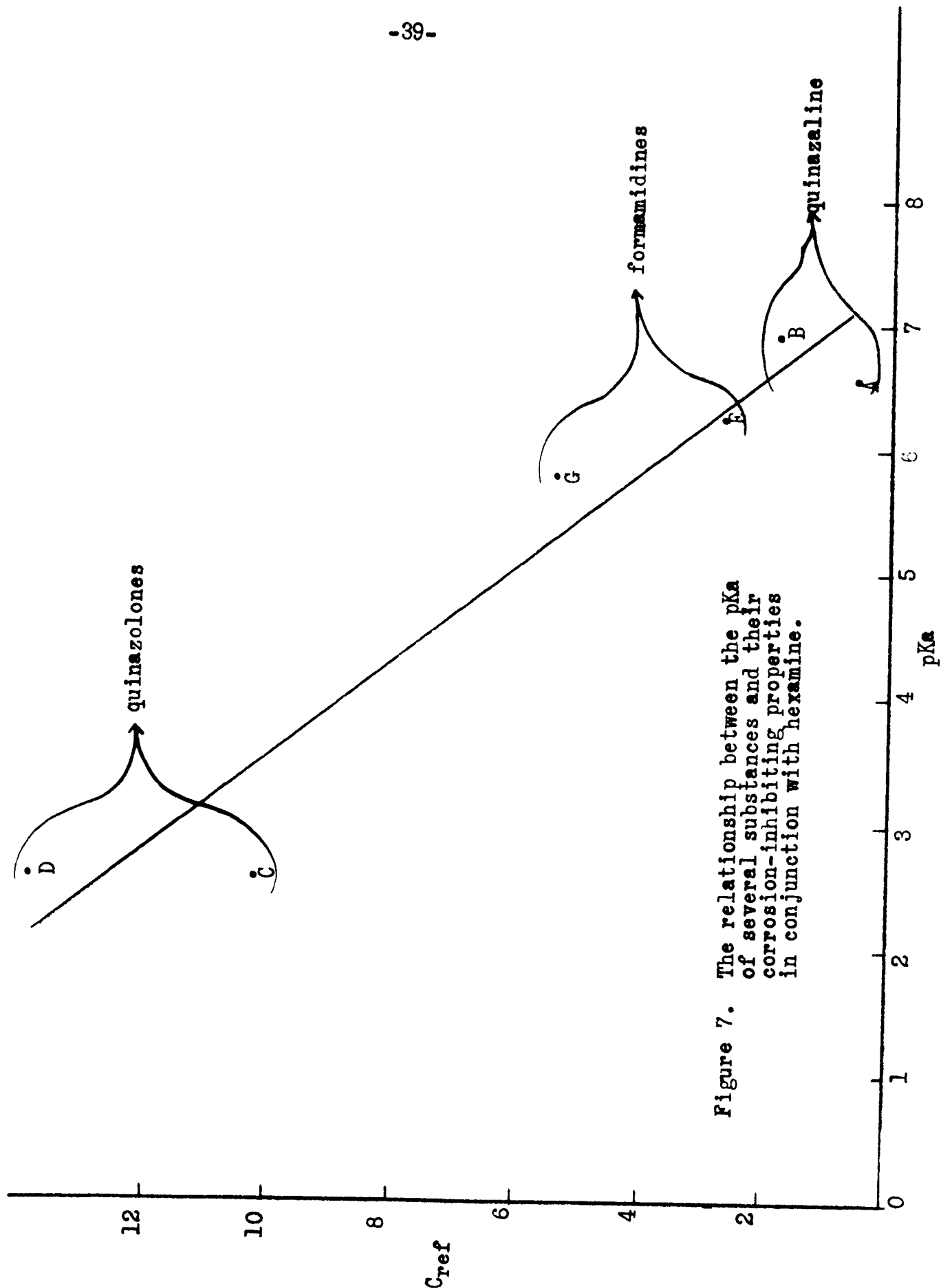


Figure 7. The relationship between the pK_a of several substances and their corrosion-inhibiting properties in conjunction with hexamine.

Figure 8. The relationship between the pK_a of several substances and their embrittlement-inhibiting properties in conjunction with hexamine.

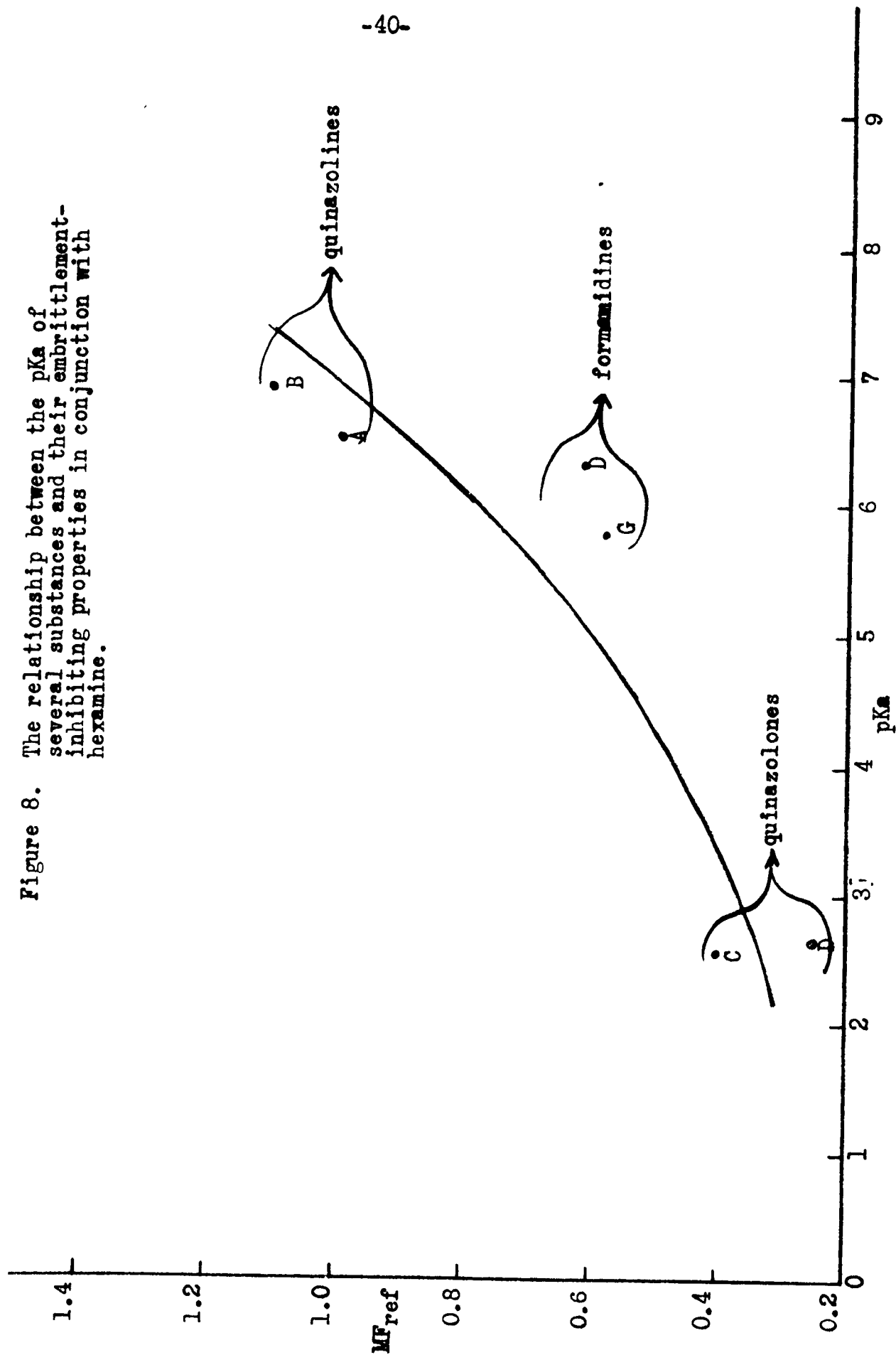
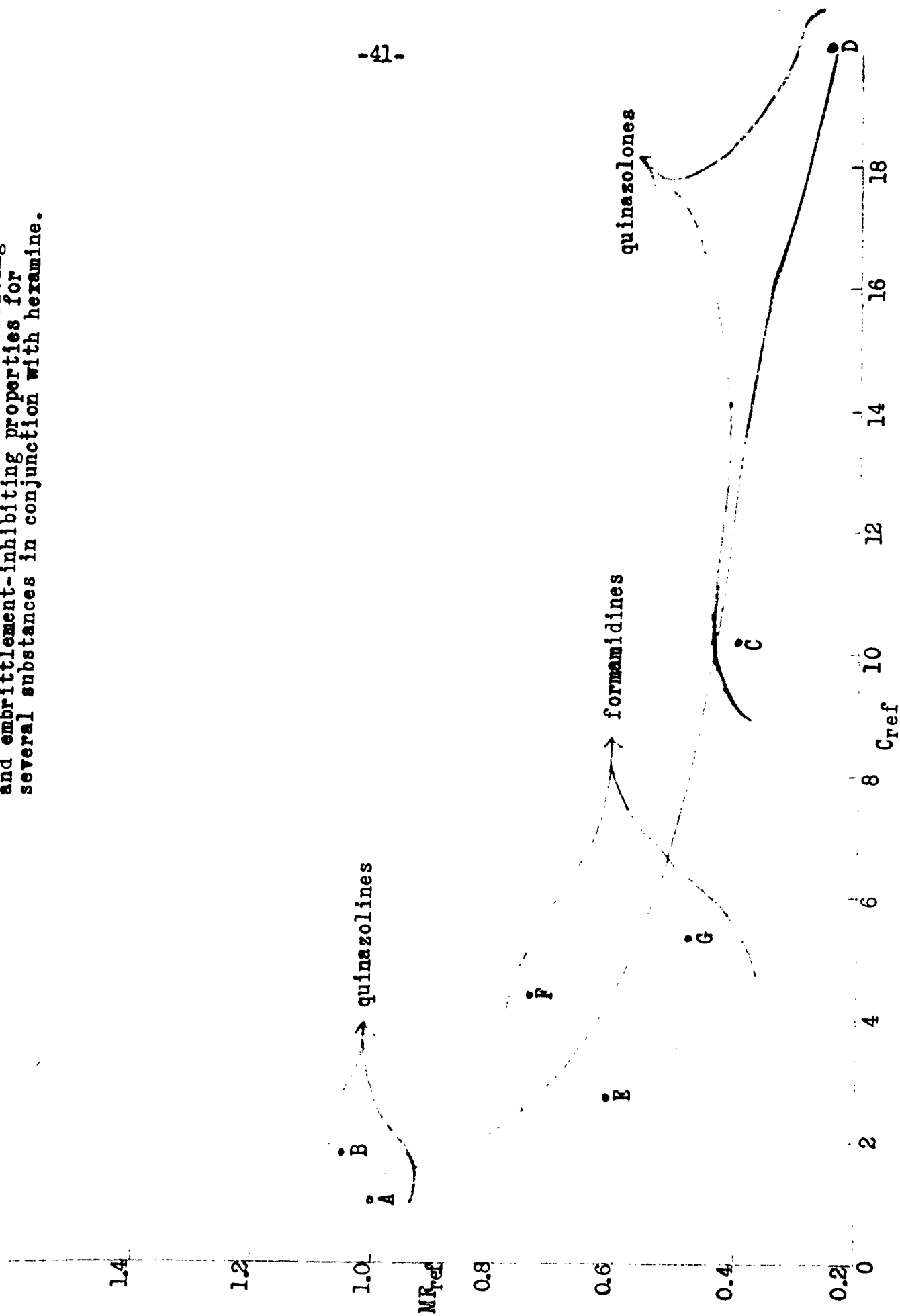


Figure 9. The relationship between corrosion-inhibiting and embrittlement-inhibiting properties for several substances in conjunction with hexamine.



III. Theory

A. Summary of Postulates and Implication of Theory of Hydrogen Embrittlement Inhibition.

This theory was presented in its entirety in a separate report. See report No. CCL No.88 from Coating and Chemical Laboratory of Aberdeen Proving Ground.

Briefly, it is postulated that atomic hydrogen is produced in steel at the cathodic sites by loss of the water envelope from the hydronium ion and by picking up an electron but that this atomic hydrogen enters through anodic areas. It is postulated also that the efficiency of the inhibitor to prevent hydrogen embrittlement is proportional to the fraction of the anodic area covered by the inhibitor and to the strength of the adsorption bond it forms on these sites (free energy decrease on adsorption). This last postulate has been modified, due to work done at Rutgers subsequent to the report, fraction of anodic area covered being changed to effective fraction of anodic area covered, this effective area being identified as the sites at which adsorption of hydrogen occurs by converting the atomic hydrogen to a proton with loss of an electron to the anodic site, and to probably be identical to those sites in the (112) slippage planes made available by dislocations, as described by P.G. Bastien in Physical Metallurgy of Stress Corrosion Fracture, P. 311. Time was not available to investigate this postulate experimentally prior to expiration of contract. A mathematical consequence of the theory (see CCL No.88) is that the higher the pKa of an inhibitor containing the amidine linkage and its Moore-Fatigue inhibitory power in the

presence of 0.5% hexamine was derived.

A corrosion inhibition theory is also described, based on the postulate that when inhibitor adsorption of mixed type occurs, corrosion inhibition is due to the potential set up between the adsorbed cathodic and anodic species and that this potential opposes the corrosion potential. The original report should be consulted for details of this derivation.

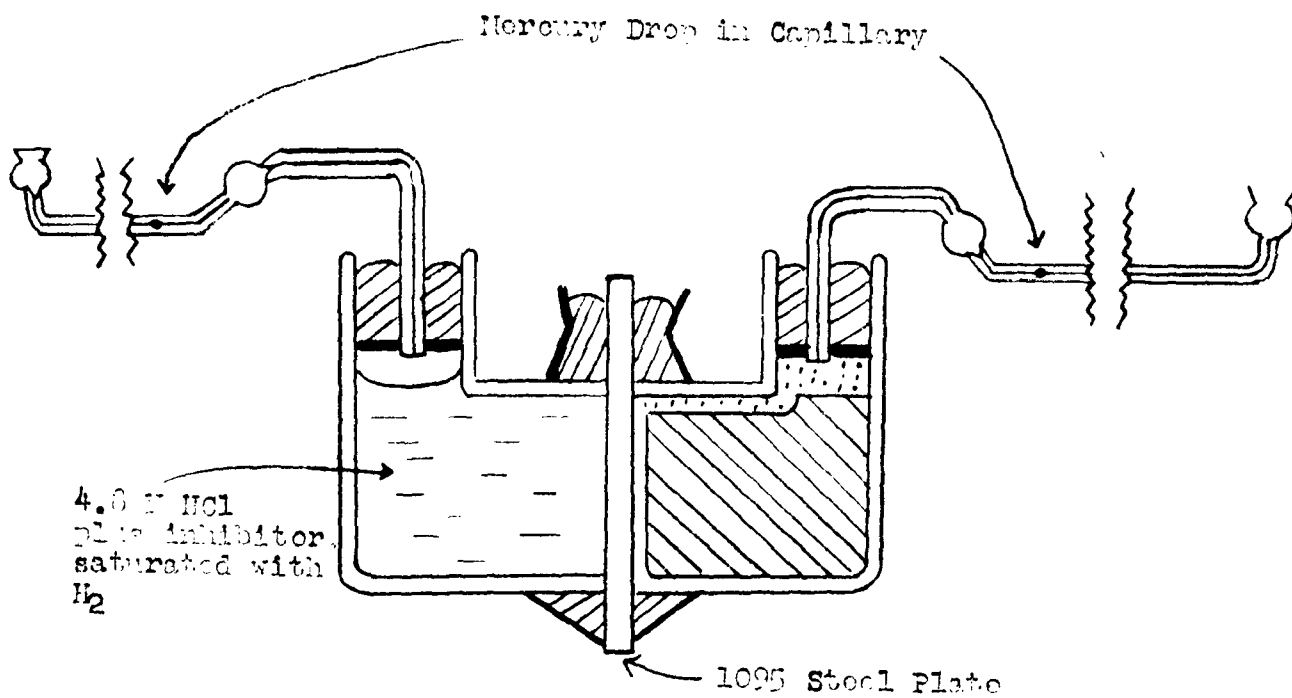
B.1. Determination of ratios of Hydrogen evolved/Hydrogen diffused into metal.

One of the deductions which follows from this theory is that the ratio of "H evolved/H diffused into metal" should be greater when an inhibitor is present than otherwise. Furthermore, in a series of substances containing the amidine-linkage the highest ratio should be observed when inhibitor with the highest pKa value is present.

The apparatus shown in Figure 10 was developed after considerable testing to measure simultaneously hydrogen evolved and hydrogen diffused. The major difficulty was to design the apparatus so that small amounts of diffused hydrogen could be measured. It was assumed that the hydrogen in the metal is a direct function of the amount diffusing through. Preliminary measurements were made but before reliable data could be obtained to test the theory the contract was terminated.

To check the assumption that the hydrogen diffusing through the metal is a direct function of hydrogen in the metal parallel investigations were begun at the same time involving high vacuum

Figure 10. Apparatus for Simultaneous Measurement of Hydrogen Diffusion and Evolution



Hydrogen gas moves mercury drop along calibrated capillary and is thus measured.

Tin and sand reduce volume, minimizing error due to changes in temperature or atmospheric pressure.

Hydrogen contacts only materials which do not absorb it.

extraction of gases after pickling, measurement of the resulting volume, and then mass spectrographic analysis. The procedure used was the following:

The steel specimen was pickled, then washed in methanol, and air dried for 15 minutes. The specimen was then placed inside a fused quartz tube which was attached to a high vacuum system. A nichrome wire coil wrapped around the tube was the heat source and a thermocouple probe was in contact with the steel specimen. The quartz tube was evacuated and, at the same time, heated to 400°C. After 15 minutes, the pressure was about 0.01 micron of Hg, and the quartz tube was then isolated from the pump, but a McLeod gauge was still connected to the tube. The volume of the quartz tube was known, and the measured pressure therefore enabled the amount of evolved gas to be calculated, once the system has cooled to room temperature. The pressure generally rose to its maximum in about 24 hours. For mass spectrographic analysis, samples of the evolved gas could be taken by means of a detachable bulb.

As in the previous case the contract was terminated before the critical data for testing the theory were obtained. One significant result obtained from the analysis of the extract from a pickled and unpickled specimen is illustrated in the data shown in Table 17. It can definitely be seen that hydrogen enters the steel during pickling. The presence of the other substance is probably due to adsorbed surface films of water, air constituents, and grease (hydrocarbons).

Table 17

Gas Extracted from Unpickled and Pickled Specimens Using the
Vacuum Extraction Procedure

<u>Gas</u>	<u>Unpickled</u>	<u>Pickled</u>
H ₂	0 %	78 %
H ₂ O	38.3	14.3
N ₂	37.2	2.2
O ₂	9.5	0.5
CO ₂	13.4	5.0
A	1.0	"trace"
EtOH	0.7	"trace"
MeOH	0	0
Hydrocarbons	0.6	"trace"
Acetylene	0	0
CH ₄	0	0

The following comment on the method proposed to test the theory was made by Dr. Rosenfeld in a private communication: "It is not clear that the theory leads to the conclusion that the ratio of hydrogen evolved to diffused should be measurably greater for inhibited acid, as the effect would be complicated by the fact that removal of a cathodic electron by the hydronium ion conversion to an atom of hydrogen without possibility of restoring the electron by reconversion to a proton at the anode would change the cathodic potential and thus interfere with hydronium ion conversion."

1. Development of a method for determining which substances "absorb atomic hydrogen" and the finding of such substances.

a. Hydrogen evolution studies.

"Uptake of Hydrogen by certain Organic Inhibitors During the Pickling of steel in Hydrochloric Acid" *

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Introduction

In the course of research in progress, under ORD 1680 and ORD 1689, DHQ (3-p-tolyl-6-methyl-3,4-dihydroquinazoline) and hexamine (hexamethylene tetramine) have been shown to inhibit increased hydrogen embrittlement of steel to an appreciable extent during acid pickling. In connection with the study of the mechanism of the action of these substances a new apparatus has been devised for measuring the volume of hydrogen evolved and the amount of iron simultaneously dissolved in the reaction of steel with an acid. It has been used to measure the uptake of hydrogen in the presence of certain organic inhibitors during the reaction of 1095 steel with 4.8 N HCl. It is hoped that this method of approach may be used to increase the understanding of the mechanism of hydrogen embrittlement of steel and, in particular, the mode of action of certain embrittlement inhibitors.

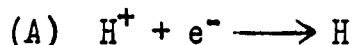
It has been generally accepted that hydrogen embrittlement in steel due to acid pickling is caused by hydrogen atoms formed at the surface of the metal which then diffuse to layers of metal beneath

* This paper was submitted for publication in "Corrosion". It is included in this report as it was submitted.

the surface.^{4,5} The rate of this diffusion into the metal and

 (4) (5) Footnote, see page 62 .

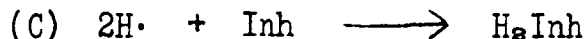
consequent embrittlement could be altered by any combination of three different processes.



This over-all rate of formation of hydrogen atoms could be slowed by any general metal attack inhibitor.

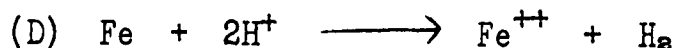


This rate of combination of hydrogen atoms to form hydrogen molecules could be accelerated, thus shortening the average time available to each hydrogen atom for diffusion into the metal.



Some additional substance, Inh, could conceivably be added whose molecules would be able to react quickly with hydrogen atoms at the surface of the metal, an acceptor thus preventing their diffusion into the steel.

The number of moles of hydrogen produced should equal the moles of ferrous ion formed as shown by the over-all equation (D). The experiments described below permit the measurement of



the hydrogen gas evolved and the amount of iron dissolved during a single reaction of a steel sample and acid. These results show the extent of reaction (C).

Experimental Method

The apparatus is depicted in Figure 11. Compartments E and G are made in one piece from pyrex glass and are immersed in a constant temperature bath. Water from this bath is also circulated through the water jacket, K, containing a 50ml. buret, I, and a comparison tube, J, which is open to the atmosphere. The Hg-levels in I and J can be altered by raising or lowering the Hg-reservoir, L. A graph paper mounted on a board is placed behind K and observed by means of a telescope from a distance of about 10 feet. The lines on the graph paper are made perpendicular with the aid of a plumb line. The hair line of the telescope is aligned with the horizontal lines on the graph paper and in turn can be used to determine when the two Hg menisci are at the same level. Except for the 1-mm capillary tube, H, all of the enclosed gas in chambers E, G, and I is maintained at the same temperature by the constant temperature bath.

The steel samples used in these experiments were half-inch diameter, cold drawn, annealed, 1095 steel rods. The surface of the samples was prepared by polishing in a drill press with No. 0 emery cloth, followed by 6/0 production paper, after which the samples were rinsed with water and absolute alcohol and then dried. The ends were painted with an acid resistant paint leaving a 6-cm length exposed.

The steel sample, D, is placed in the apparatus and acid is added to G so that no air is trapped in the tube below stopcock C. The rubber tube B and stopper with stopcock F are attached, and this

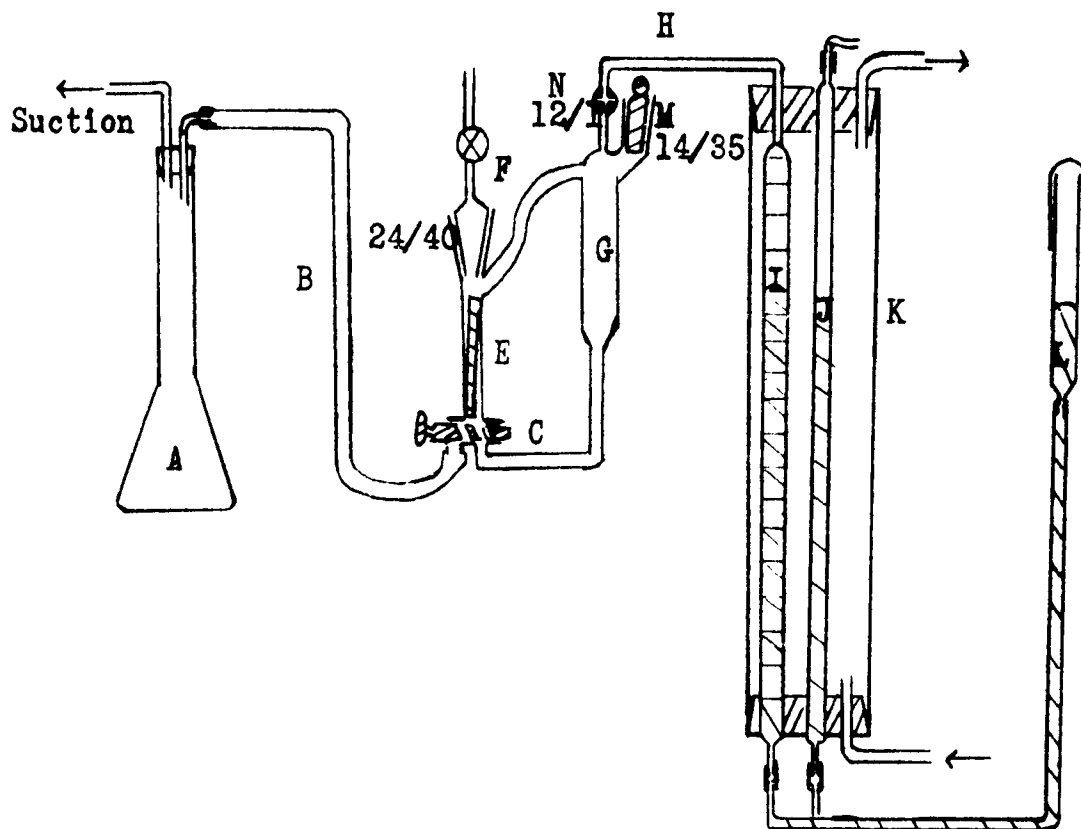


Figure 11. Apparatus for measuring the volume of hydrogen gas evolved and the amount of iron simultaneously dissolved during the reaction between an acid and a steel sample.

part of the apparatus is placed in the constant temperature bath. Before the experiment is started it is necessary to flush the system with hydrogen and to make certain that the acid has been saturated with hydrogen. For this purpose a special tube which is drawn to a small tip and which reaches to the bottom of compartment G is inserted at M; hydrogen enters at this point and exits at N. After saturating the acid with hydrogen, the tube at M is replaced with a solid glass stopper, and the buret is connected at N. Hydrogen is again passed through the system entering through B and exiting at F. After all air has been replaced with hydrogen, the stopcocks at C and F are closed. A vacuum is produced by lowering L in order to tighten all connections and to test for leaks. The system is then adjusted to atmospheric pressure, and the buret is read periodically to determine when equilibrium is reached in the apparatus. It is necessary that the gas space be nearly saturated with the vapors from the acid. This requires about one hour.

After essential equilibrium has been reached and the initial buret reading taken with the Hg-levels in I and J are the same, the stopcock at C is turned so as to admit acid from G into E sufficiently to cover the sample, after which C is closed. The time of admitting the acid is recorded as the start of the reaction. Additional buret readings may be obtained as frequently as desired by bringing the pressure to atmospheric pressure and recording the buret reading and corresponding time. The rate of the reaction may thus be followed. The atmospheric pressure should be measured at each observation. At the end of the experiment M is opened; C is turned so as to remove

acid from E thru B into volumetric flask, A, by means of suction; F is opened; and several flushings of chamber E and sample, D, are made by admitting distilled water through F. The solution in A is then diluted to volume and the iron determined by colorimetric analysis using orthophenanthroline. An adaptation of the method of Fortune and Mellon⁶ was used in which the solution was buffered with sodium

(6) See page 62.

acetate.

The experiments herein described were performed at 37.8 C. and in 4.8 N hydrochloric acid solutions. However, the final acid concentration was slightly less in those experiments in which hexamine or DHQ were added as inhibitors because of the partial neutralization of the acid by the inhibitor.

Experimental Results

The millimoles of iron are computed from the results of the colorimetric analysis. The final buret reading is obtained by extrapolating from the last two observed values to the time at which the acid was drained from the reaction vessel. If the atmospheric pressure changes during the course of the experiment, the dead volume is altered and a corresponding correction must be made in the computed volume of hydrogen. The dead volume is the volume occupied by the gas present in E, G, and I at the start of the experiment. The millimoles of hydrogen are computed from the corrected volume, the temperature, and the pressure by means of the ideal gas law. However, it is necessary first to correct the pressure by subtracting the vapor

pressure of 4.8 N HCl is calculated to be 3.49 cm Hg at 37.8 C. by interpolation from the International Critical Tables.⁷ If no hydrogen

(7) See page 62.

is taken up by the steel or by organic compounds present in the acid, then the millimoles of iron should be equal to those of hydrogen. The ratio of millimoles of hydrogen to millimoles of iron has been calculated for each experiment performed and is given in Table 18. When this ratio is significantly less than one, the uptake of hydrogen by the inhibitor is indicated. The study of this process is the main purpose of the present study.

In addition, if buret readings are made during the course of the experiment, it is possible to calculate hydrogen evolution rates. These vary by a factor of sometimes as high as two from experiment to experiment even when the composition of the solution is essentially unchanged. Nevertheless, general trends and differences are markedly apparent, and these have been condensed into Table 19. The rate during the first interval was always greater than ensuing rates in all cases except that of 0.214 M nitroethane. Those experiments in plain acid showed some tendency toward decreasing rates during the time of the experiment. On the other hand, the experiments in which hexamine was present showed marked decreases in the rates. With 0.036 M hexamine, these decreases continue over a period of 1000 minutes or more while with the higher concentrations of hexamine a more or less constant rate is reached after about 100 minutes.

Table 18 - Determination of the ratio of hydrogen evolved to iron simultaneously dissolved during the action of 4.8 N HCl, both with and without added inhibitors, upon 1095 cold rolled annealed steel rods at 37.8 C.

<u>Exp. No.</u>	<u>Fe (millimoles)</u>	<u>Ratio (H₂/Fe)</u>	<u>Inhibitor</u>	<u>Av.</u>
H-2	0.800	1.01	None	
H-3	0.943	1.05	None	
H-4	1.11	1.00	None	
H-7	1.22	1.00	None	
H-19	1.08	0.98	None	
H-35	1.39	0.98	None	<u>1.003</u>
H-10	1.09	0.92	0.036 M Hexamine	
H-13	0.725	0.91	0.036 M Hexamine	
H-15	0.735	0.87	0.036 M Hexamine	
H-17	0.715	0.82	0.036 M Hexamine	
H-20	0.340	0.85	0.036 M Hexamine	<u>0.874</u>
H-43	0.759	0.56	0.071 M Hexamine	
H-45	1.152	0.65	0.071 M Hexamine-precoated	
H-46	1.32	0.78	0.071 M Hexamine	
H-47	1.02	0.74	0.071 M Hexamine-precoated	<u>0.682</u>
H-28	1.61	0.47	0.214 M Hexamine-3.9 N HCl	
H-29	1.44	0.40	0.214 M Hexamine-3.9 N HCl	<u>0.435</u>
H-32	1.10	0.18	0.71 M Hexamine-2 N HCl	
H-42	2.26	0.13	0.71 M Hexamine	
H-40	2.79	0.15	0.71 M Hexamine-5.1 N HCl	<u>0.153</u>
H-37	0.568	0.98	0.214 M Formaldehyde	
H-38	0.521	0.88	0.214 M Formaldehyde	
H-39	0.623	0.91	0.214 M Formaldehyde	<u>0.92</u>
H-23	0.210	0.97	0.0063 M DHQ	
H-24	0.137	0.97	0.0063 M DHQ	
H-25	0.131	1.01	0.0063 M DHQ	<u>0.98</u>
H-12	0.094	1.01	0.0063 M DHQ and 0.036 M Hex.	
H-16	0.148	0.87	0.0063 M DHQ and 0.036 M Hex.	
H-18	0.103	0.99	0.0063 M DHQ and 0.036 M Hex.	
H-21	0.190	0.94	0.0063 M DHQ and 0.036 M Hex.	
H-22	0.104	1.01	0.0063 M DHQ and 0.036 M Hex.	
H-26	0.129	1.03	0.0063 M DHQ and 0.036 M Hex.	
H-27	0.105	1.00	0.0063 M DHQ and 0.036 M Hex.	<u>0.978</u>

Table 18 (Con't)

<u>Exp. No.</u>	<u>Fe (millimoles)</u>	<u>Ratio (Hg/Fe)</u>	<u>Inhibitor</u>	<u>Av.</u>
H-30	3.15	0.30	0.214 M Nitroethane	
H-31	3.50	0.15	0.214 M Nitroethane	
H-36	1.91	0.24	0.214 M Nitroethane	
H-44	3.52	0.12	0.214 M Nitroethane	<u>0.202</u>
H-33	0.50	0.45	0.214 M Nitroethane and 0.0063 M DHQ	
H-49	0.67	0.24	0.214 M Nitroethane and 0.0063 M DHQ	
H-50	0.80	0.17	0.214 M Nitroethane and 0.0063 M DHQ	
				<u>0.283</u>

Table 19 - Rates of evolution of hydrogen gas by 1095 cold rolled annealed steel rods in 4.8 N HCl at 37.8 C. both with and without inhibitors. The rates are given in units of $\text{H}_2/\text{cm}^2 \text{ min.}$ In most cases an approximate range indicated because the measured values vary from one experiment to another.

<u>Inhibitor</u>	<u>Rate</u>	<u>Remarks</u>
None	27-45 20-25 12-20	initial rate 5 - 15 minutes 20 - 60 minutes
0.036 M Hexamine	14-30 1-3 0.5-1 0.35-0.40	initial rate 10 - 30 minutes 200 - 700 minutes 1100 - 1400 minutes
0.071 M Hexamine	12-15 2-3 0.5-0.7	initial rate 10 - 30 minutes 200 - 1100 minutes
0.214 M Hexamine	8-9 1-2 0.4-0.5	initial rate 10 - 30 minutes 100 - 1500 minutes
0.71 M Hexamine	1-2 0.3-0.4	initial rate 100 - 1000 minutes
0.214 M Formaldehyde	6-9 3-5 2-3	initial rate 10 - 60 minutes 60 - 180 minutes
0.0063 M DHQ	1.7-2.5 0.2-0.4	initial rate 10 - 300 minutes
0.0063 M DHQ and 0.036 M Hexamine	2-9 0.04-0.10	initial rate 30 - 2000 minutes
0.214 M Nitroethane	4-9	rate is essentially constant, 0 - 120 minutes
0.214 Nitroethane and 0.0063 M DHQ	2-2.5 0.1-0.2	initial rate 15 - 1200 minutes

Discussion of Results

On the basis of the accuracy of the various measurements and corrections involved in an experiment, the expected uncertainty in the calculated ratios is less than 0.02 in most of the experiments of Table 18. In several experiments the actual agreement is poorer than this. Several possible additional causes might contribute to variations in the ratios. If, for any reasons, the samples have an oxide film on their surfaces as proposed by Todt,^{8,9} the ratio will be

 (8) (9) See page 62.

decreased. Since the results for plain acid and acid containing DHQ are close to 1.00 no large systematic error is present from this source. The experiments varied in duration as is indicated by the variation in the millimoles of Fe among experiments with the same inhibitor in Table 18; however, there is no trend relating the length of the experiment and the uptake of hydrogen. The time that the system was maintained, after passing hydrogen through it but before starting the reaction, varied between experiments. This time spent in waiting for attainment of equilibrium inside of the apparatus is probably accompanied by some reaction of the moist acid vapors and the polished steel surface. Sometimes a visible slight discoloration of the surface appears. The extent of this attack will vary somewhat from experiment to experiment, through introducing another variable which tends to make the ratios less than 1.00. This preliminary metal attack is believed to be quite small because the ratios are still close to 1.00 with plain acid.

Even with these possible sources of error the data of Table 18 clearly shows differences in uptake of hydrogen with concentration and composition of the inhibitors used. Solutions containing hexamine definitely take up hydrogen, and the fraction of hydrogen taken up increases with increasing concentration of hexamine. If DHQ is added to the solution containing hexamine, it decreases slightly the extent of hydrogen uptake. This negative effect of DHQ is also shown in its use with nitroethane. Most of the experiments using DHQ and hexamine together indicate that no measurable amount of hydrogen reacts with the inhibitors. It seems that the DHQ is absorbed on the surface more strongly than is the hexamine, and thus displaces it and prevents the uptake of hydrogen by hexamine or its hydrolysis product, formaldehyde. The experiments with 0.214 M and 0.71 M hexamine solutions indicate that the surface is not completely covered with a monolayer at the lower concentrations and perhaps not even at a concentration of 0.71 M. Nitroethane, which has high reactivity toward atomic hydrogen, was examined in the apparatus of Figure 11. It reacts with a greater fraction of the hydrogen than does an equimolar concentration of formaldehyde or the 0.036 M hexamine solution, which, if completely hydrolyzed, would form 0.214 M formaldehyde. Even in the presence of DHQ from 55 to 80 per cent of the hydrogen formed is taken up by the nitroethane. Table 19 shows that the metal attack rate, which corresponds to the rate of production of hydrogen atoms, is very small when DHQ is present even in combination with nitroethane.

One other interesting fact observed is found in Table 19. In most cases a fairly constant rate of metal attack is attained soon

after the beginning of the reaction; however, with 0.036 M hexamine the reaction continues to decrease in rate even after 700 minutes. It finally reaches a rate approximately equal to that attained in 0.214 M hexamine solution in only 100 minutes. This slow decrease in rate can hardly be attributed to the time required to form an equilibrium adsorbed layer of inhibitor on the surface. It seems that with hexamine some other slower reaction must be taking place in the main body of the solution and not at the solution-metal interface. Perhaps the hydrolysis of hexamine to ammonium chloride and formaldehyde is slow enough to account for this delay in the inhibiting effect.

The initial rates are considerably higher than those obtained after a few minutes. This type of behavior has previously been observed during the first few seconds by Todt and co-workers.^{9, 10}

(10) See page 62.

Wickert and co-workers¹¹ have measured the rate of solution of iron

(11) See page 62.

in hydrochloric acid both with and without hexamine during the first few seconds. They found that the rate even during the first second was much greater than during later seconds. The effect is larger when an inhibitor is present, and this high initial rate followed by a much lower rate of reaction is probably caused by the time required to form an adsorbed layer of inhibitor on the surface of the steel.

On the basis of these results and in terms of the three reactions mentioned in the second paragraph of the introduction, one can say

that DHQ would be eminently good at slowing down the rate of production of hydrogen atoms, reaction (A), simply by its over-all ability as a metal attack inhibitor. Table 19 indicates that the rate of hydrogen evolution is out by a factor of about 50 by DHQ alone and by a factor of about 200 by the combination of DHQ and hexamine. Table 18 shows that DHQ has no perceptible power to react permanently with hydrogen atoms, reaction (C), and thus cannot inhibit embrittlement in this manner. The results of this study afford no answer to the extent of reaction (B). On the other hand, hexamine could inhibit embrittlement by means of reaction (C) unless interfered with by DHQ, and the results of Table 18 indicate the reality of this interference. Hexamine can also contribute to the inhibition of reaction (A), especially when in combination with DHQ. Nitroethane should be very effective at inhibiting embrittlement by means of reaction (C), and furthermore the interference of DHQ is much less than in the case of hexamine. Further work at other concentrations is necessary before it is possible to say what combination of these inhibitors would be expected to be best for the inhibition of hydrogen embrittlement. Also, a knowledge of the rate of combination of hydrogen atoms to form molecules and the rate of diffusion into the metal is necessary in order to completely answer the question of the extent of embrittlement inhibition in terms of the theory briefly outlined in the introduction. If reaction (B) is important in shortening the free lifetime of hydrogen atoms, then a method needs to be devised for the study of this reaction.

Conclusions - The new apparatus and method described on the preceding page have produced results which show that some inhibitors react with hydrogen at the surface of steel in an acid solution. It will be possible with the aid of this method to determine to what extent the action of pickling embrittlement inhibitors is due to the combination of inhibitor with hydrogen atoms as they are formed.

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- (10) F. Todt, Arch. Metallkunde, 1, 249-51 (1947).
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* References have been numbered with respect to their position in the final report rather than in this report.

b. The Oxide Film Assumption

An important assumption made in the preceding paper was that the contribution of the amount of iron in the oxide film to the amount of iron found in the analysis is negligible. This assumption was tested in the following manner.

Steel specimens like those used in the hydrogen evolution studies were allowed to stand in air for various lengths of time after having been etched 30 seconds in HCl to remove any original film. The subsequent weight losses of such specimens following a 5 second immersion in N HCl were measured. The data are presented in Table 20.

Table 20

<u>Minutes in Air</u>	<u>Iron dissolved (mg)</u>
0	0.41
1	0.41
10	0.60
40 or longer	0.61

The contribution of the oxide film is believed to be the difference between "0" time and "40 or longer", or about 0.20 mg. Such a contribution to the total iron analyzed in the hydrogen evolution studies is negligible because it is within the experimental error.

c. The Hydrogen Absorption Assumption

Since the reduction of the inhibitor was not demonstrated directly, one could argue that the metal might have absorbed the hydrogen. Further, in the absence of the inhibitor the ratios

obtained indicated that all the hydrogen formed was evolved. This might be interpreted to mean that no hydrogen is absorbed by the metal under these conditions. In order to clarify these two points the quantities of hydrogen absorbed by the steel under the conditions under which the hydrogen evolution experiments were performed were measured.

The procedure used was that reported by Darken and Smith¹⁸

(12) L. S. Darken and W. P. Smith, Corrosion, 5, 1 (1949).

in which 95% of the hydrogen absorbed was measurable. The steel rod specimens, after pickling, were washed with methanol, dried, and placed in a beaker of mercury. A partial vacuum was obtained by attaching a water aspirator to a mercury-filled buret inverted over the specimen. This partial vacuum is a supplemental improvement over the Darken and Smith apparatus. The beaker was heated to 170°C. in an oil bath for approximately five (5) hours. The data obtained are presented in Table 21. In addition the average volume of hydrogen evolved and that unaccounted for in Anderson's hydrogen evolution experiments are also presented.

The concentrations used were the maxima reported in the hydrogen evolution studies. It can be seen that for the inhibited solutions the amounts of hydrogen absorbed are either not measurable or, in the case of 0.214 M nitroethane, cannot account for the discrepancy in the hydrogen evolution experiments. The hydrogen absorbed in uninhibited acid solution is within the experimental error observed in measuring the total amount of hydrogen evolved in the experiments

on this point.

Table 21

<u>Inhibitor Added to 4.8 N HCl</u>	<u>Random Precision Error in Anderson's Volumes in cc.</u>	<u>Volume of Gas Extracted From Steel in cc.</u>	<u>Data on H₂; cc's (Anderson)</u>	
			<u>Equiv. to Fe Dis.</u>	<u>Act. Coll.</u>
0.0063 M DHQ	± 0.11	0.00	35.6	34.9
0.71 M Hexamine	± 0.10	0.00	45.9	7.0
0.214 M Nitroethane	± 5.6	0.08	67.6	13.5
None	± 0.25	0.17	24.4	24.4
---	---	0.00		

All volumes at STP

d. Evidence that nitroethane is reduced.

In the preceding section it was shown that the disappeared hydrogen was not absorbed by the metal. The next step was to show that it was absorbed by the organic substance present. The following work establishes that nitroethane is reduced.

The nitroethane pickling solution was evaporated to dryness under an aspirator vacuum. Similarly, a sample of pickling solution which had not been used for pickling was evaporated to serve as a "control". A few drops of ethylamine were added to a third sample of unused

pickling solution and evaporated. This was the "standard".

On each of the three solid residues three tests were made:

- (1) The sample was fused with fluorescein chloride reagent (3',6'dichlorofluoran) and ZnCl_2 ; amines give a dye which remains fluorescent when acidified.¹³

(13) F. Feigl, Spot. Tests. II., 192, Elsevier Pub. Co., New York (1954).

- (2) The sample was heated with furfural in acetic acid; amines give an orange dye.¹³

- (3) The sample was dissolved in acetic acid and sodium nitrite was added; amines give off N_2 gas.¹⁴

(14) J. B. Niederl, Micro Methods of Org. Anal., 273, John Wiley and Sons, New York (1942).

The results are shown in Table 22.

Table 22

<u>Test</u>	<u>Control Result</u>	<u>Used Pickling Solution Result</u>	<u>Standard Result</u>
Fluorescein	Negative	Definitely positive	Definitely positive
Furfural	Negative	Probably positive	Definitely positive
N_2	Negative	Probably positive	Definitely positive

It is concluded that amine was present and therefore, that reduction has occurred.

2. Evaluation of a mixture which was predicted to be a superior hydrogen embrittlement inhibitor on the basis of previous work.

a. Moore-Fatigue testing of nitroethane and DHQ.

It would appear from the hydrogen evolution studies that a mixture of 0.15% DHQ and 1.5% nitroethane should be a superior to a mixture of 0.15% DHQ and 0.5% hexamine as an embrittlement inhibitor. The former mixture both inhibits corrosion and seems to absorb a considerable proportion of the atomic hydrogen produced. DHQ-hexamine mixture does not appear to absorb atomic hydrogen.

The effectiveness of the mixtures was determined using two types of experiments, Moore-Fatigue and "diffusion potential". The data are presented in Tables 23 and 24. The data shows that at best this mixture is as good as 0.15% DHQ. In addition according to the diffusion potential data nitroethane accelerates hydrogen diffusion. These results seem to indicate the absorption of atomic hydrogen by a substance does not contribute to inhibition. Another possibility exists, namely, that nitroethane is not reduced by atomic hydrogen as had been assumed. An alternative mechanism for its reduction is discussed in the following section prepared by Professor Donald B. Denney of the School of Chemistry at Rutgers University.

Table 23 - Moore-Fatigue Results

<u>Treatment</u>	<u>MF_{ref}</u>
0.15% DHQ - 0.5% Hexamine	1.0
0.15% DHQ - 1.5% Nitroethane	0.4
0.15% DHQ	0.4

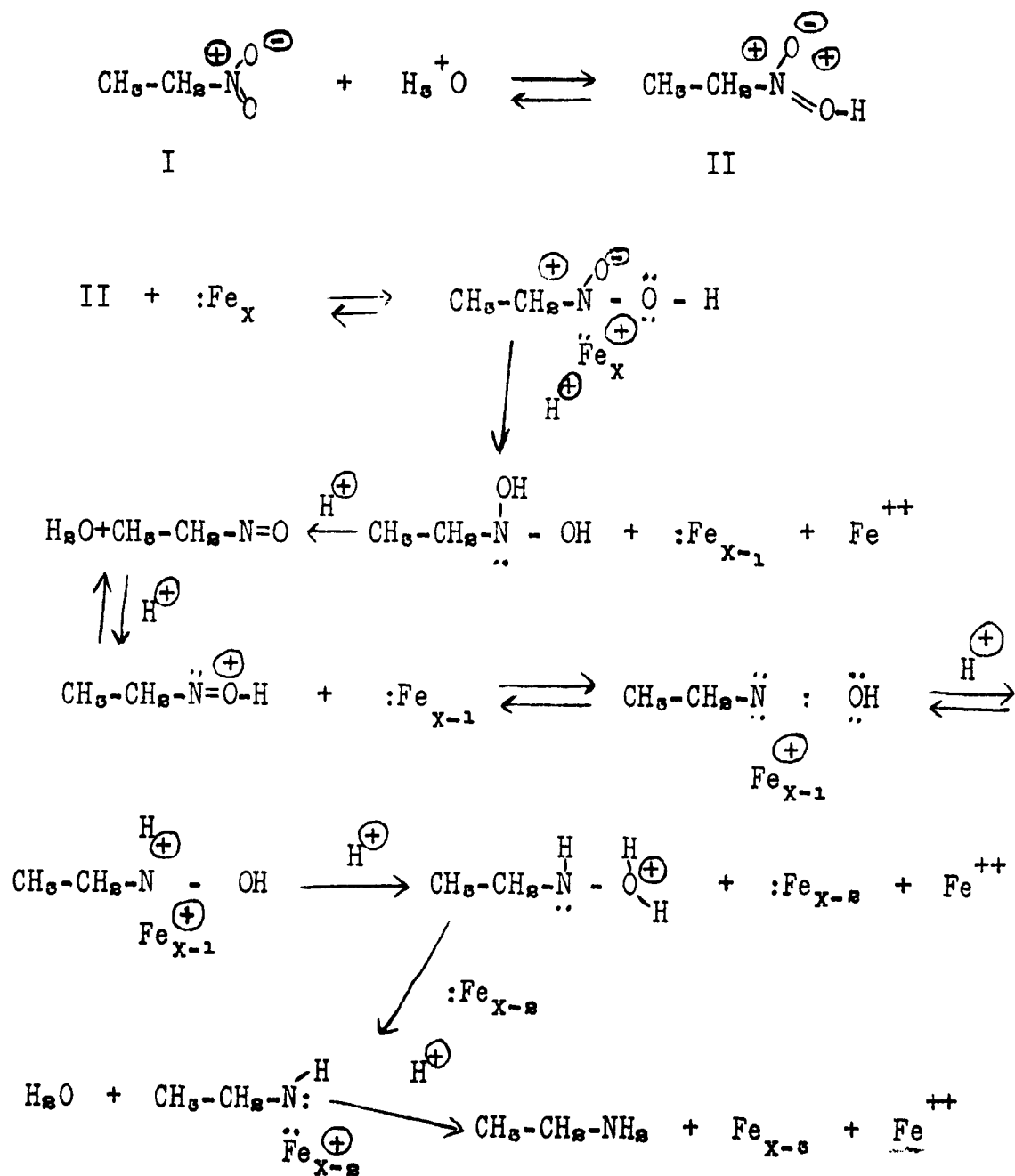
Table 24 - Diffusion Potential Results

<u>Treatment</u>	<u>Mean time-lag</u>	<u>Standard Deviation</u>
None	7.2	± 0.5
1.6% nitroethane	5.0	± 0.5
0.15% DHQ	21.4	± 0.7
0.15% DHQ - 0.5% Hexamine	34.3	± 2.2
0.15% DHQ - 1.5% Nitroethane	15.3	± 4.9

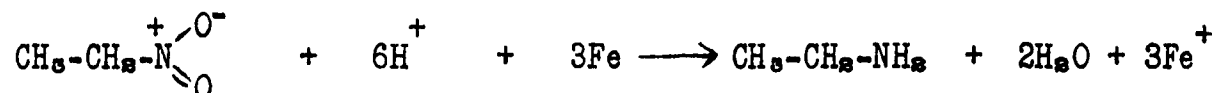
b. Proposed mechanism for reduction of nitroethane.

The mechanism of the reduction of organic substances by dissolving metals has received little quantitative study. Fortunately within the last few years several important ideas have emerged from the confusion which has existed in the past. Firstly, the concept of nascent hydrogen acting as the reducing agent has been effectively eliminated as a cogent possibility. The most recent and acceptable theory suggests that electrons from the metal are trans-

ferred directly to the unsaturated group of the substrate to give ions or radicals which subsequently react to give products. The example of interest here is the reduction of nitroethane. This can be formulated in the following manner --



The overall process is represented by the following equation -



Firstly it should be pointed out that the steps written above for the mechanism of the reduction are speculative and several variations are possible. The important thing to be noted is that this mechanism or its variations do not require attack on the metal by hydrogen ion. It should also be noted that the reduction process does not inhibit hydrogen ion attack on the steel except for a competition between the nitroethane and hydrogen ion for the metal. Since these are both fast processes, one would expect that the overall rate of attack would be faster for the mixture than for acid alone. This is the observed effect! Since the reduction does not appreciably inhibit the metal attack by acid or suppress the formation of chemisorbed hydrogen, it is not surprising that there is no inhibition of hydrogen embrittlement under these conditions. If the above ideas are accepted it becomes clear that reducible substances will not necessarily act as hydrogen embrittlement inhibitors.

c. Verification of Dr. Denney's mechanism for the reduction of nitroethane.

Dr. Denney's ideas were tested in the "diffusion potential" experiments by comparing the behavior of nitroethane and hydrogen peroxide, which is known to be reduced by atomic hydrogen. The following data were obtained from solutions in the "standard pickling solution".

Table 25

<u>Treatment</u>	<u>Mean Time-lag</u>	<u>Standard Deviation</u>
None	7.2	± 0.5
3% H_2O_2	12.0	± 4.2
1.6% Nitroethane	5.0	± 0.5

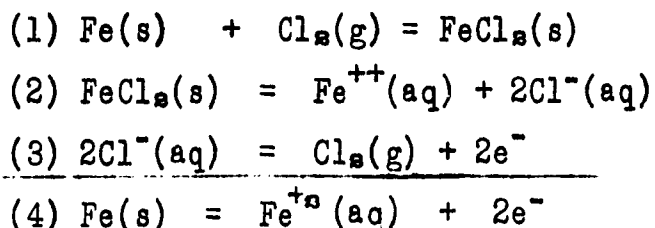
Thus H_2O_2 acts as an inhibitor whereas nitroethane acts as an accelerator. This is consistent with the concepts proposed by Dr. Denney. Unfortunately the effectiveness of H_2O_2 was not tested with respect to embrittlement inhibition because of lack of time. Therefore, the basic question posed in these studies has been left unanswered-- Are substances which absorb atomic hydrogen good embrittlement inhibitors?

B. The Reversible Electrode Potential of Metallic Iron.

The value of the reversible iron electrode potential, E°_{Fe} , has been the subject of considerable controversy recently. Several different values have been reported. All of these values were derived from electrochemical measurements in which an iron electrode was used. We believed that the lack of reproducibility was due to the corrosion currents on the iron rod. A method was devised which, it was thought, would eliminate this effect and the electrode potential was measured. The following paper is based upon the results obtained. It has not been submitted for publication. The values obtained are considerably different from those of other authors and the differences have not been adequately explained. It was decided therefore to check the

values by using an entirely different method for determining the E°_{Fe} .

The method proposed was to derive E°_{Fe} indirectly, by calculating the E°_{Fe} from a series of equilibria which are not based upon Fe electrode measurements. The following series is under study-



The necessary free energy data for (1) and (3) are in the literature. The stumbling block is (2) for which, thus far, data have not been found. If such data are not available either such measurements will be carried out or an alternate series of equilibria will be devised for which data are available.

"The Reversible Electrode Potential of Metallic Iron Without Local Action Currents" by Daniel Shanefield and Leonard Dauerman. School of Chemistry, Rutgers, The State University.

The open-circuit potential of an iron electrode is usually not the reversible potential of the reaction $\text{Fe} \longrightarrow \text{Fe}^{++} + 2\text{e}$. In acid solution, because of local action currents, iron continues to dissolve at the open-circuit potential. The reversible electrode potential was measured by extrapolating a polarization curve of iron to the point of zero local action current. Current densities were determined from the amounts of ferrous ion produced rather than from electrical measurements of applied current. A polarization curve of hydrogen evolution on iron was similarly determined, the current density

being calculated from the rate of hydrogen gas evolution.

Metals which react directly with water cannot be used to make reversible electrodes in their aqueous solutions unless special methods are used.¹⁵ In the electrode system $\text{Fe} \rightarrow \text{Fe}^{++} + 2\text{e}$, iron can dissolve even at the open circuit potential, and therefore, that is not the equilibrium or reversible potential. Electrons from the iron reaction travel as local action currents through the metal to sites where a side reaction, $2\text{H}^+ + 2\text{e} \rightarrow \text{H}_2$, takes place. The iron and hydrogen reactions can each be considered as half-cells. The internal resistance of each half-cell is mainly due to polarization and is schematically represented in Figure 12. If the activity of H^+ is unity, then the voltage of C_H is zero, as in Figure 13a. Because of polarization, we must still consider R_a , and the two resistances make up a voltage divider. When the usual cell is set up to measure the potential of metallic iron, it is E°_Fe which is sought for free energy calculations, but E_a is actually measured.

Various methods have been used to determine E°_Fe itself. The metal can be amalgamated, and the high overvoltage of hydrogen on mercury will then raise R_a , causing E_a to approach E°_Fe .^{16,17} Or, the electrolyte can be made basic, in which case the hydrogen ion concentration is too small for the side reaction.¹⁸

In these methods, however, the adsorbed film may be different from that of the more interesting case of pure metal in neutral or acid solution. Therefore the potential sought may differ from the potential measured,¹⁹ even though the hydrogen reaction is eliminated.

The method described here involves passing an applied current

Figure 12a

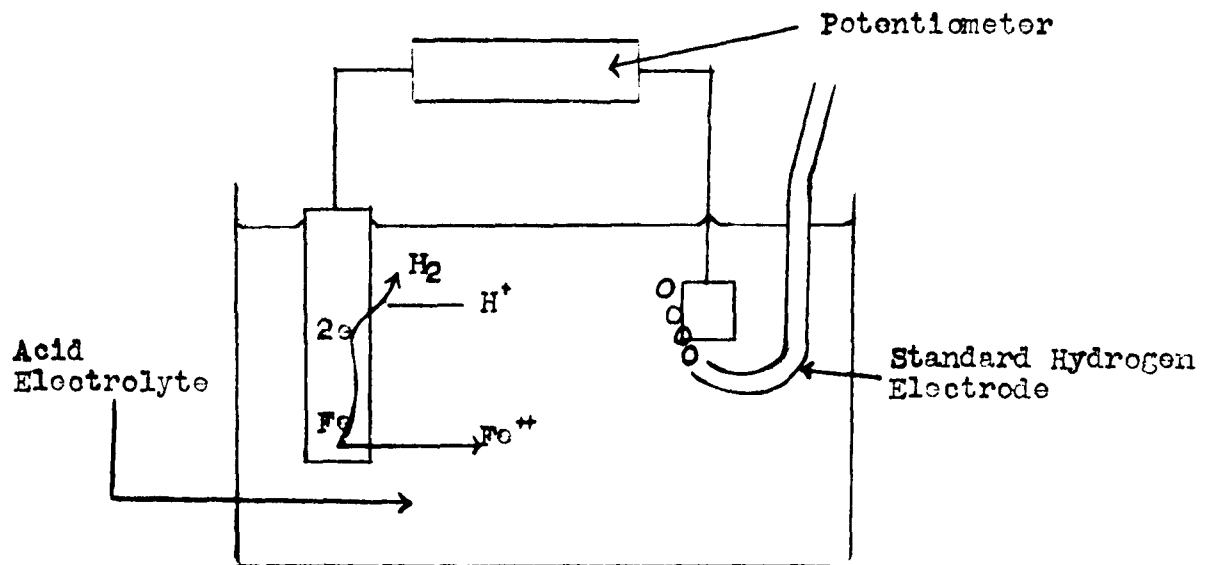
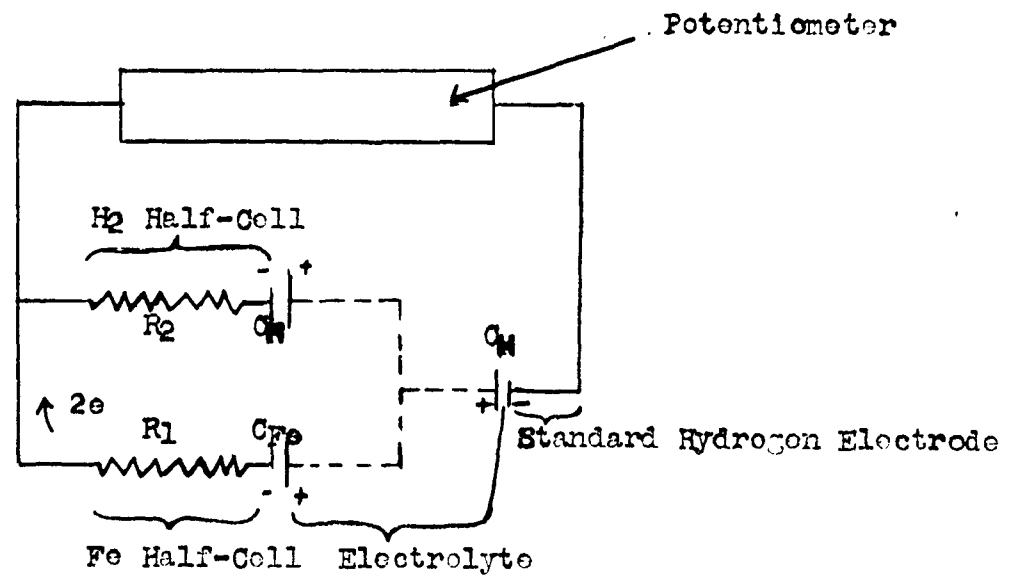


Figure 12b



from an outside battery, C_{App} , through R_s , as in Figure 13b. The outside current is increased until no more current flows through R_1 (no iron dissolves), at which point $E_s = E_{Fe}$. C_{App} is attached at A to the iron electrode and at B to an auxiliary platinum electrode placed in the electrolyte.

In previous studies of the overvoltage of hydrogen on iron, the measurements almost always involved only the applied current (through C_{App}). However, this is not all of the current which produces hydrogen (through R_s), since there is additional current from C_{Fe} . In order to determine the true hydrogen-producing current, the author measured the volume of hydrogen gas produced per unit time. This can be done even when the applied current is zero or reversed. In the latter case, the overvoltage can be extrapolated to the point of zero current through R_s , even in corrosive electrolytes.

Experimental

As illustrated in Figure 14, an Armco iron rod having an exposed area of 24 sq. cm. was suspended in a solution of Reagent Grade 1M HCl. Further purification of materials was not done since the investigation was concerned with electrochemical methods rather than with accurate absolute magnitudes. The iron rod was degreased and then pickled to remove the cold-worked and oxidized surface. The electrolyte was always taken from the same batch, which had been de-aerated with hydrogen and kept under a hydrogen atmosphere. Plastic film was spread over the apparatus, and a hydrogen atmosphere under very slight pressure was kept over the electrolyte during operations.

Figure 13a

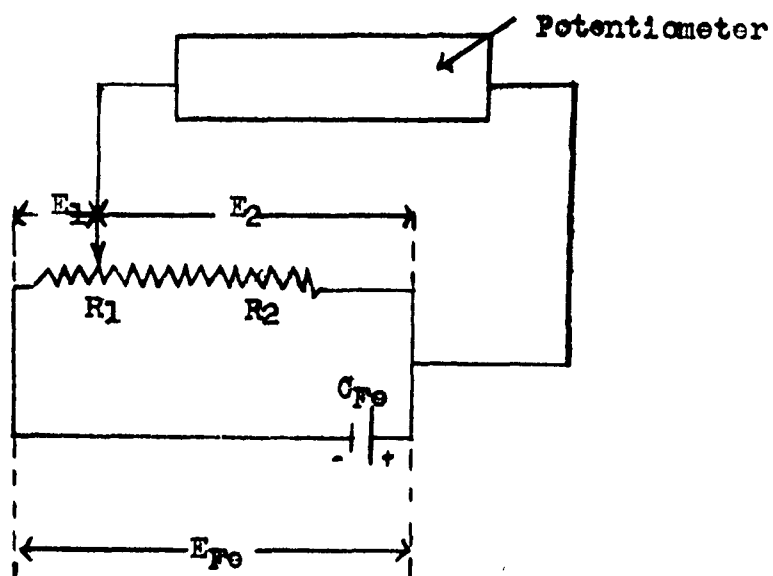


Figure 13b

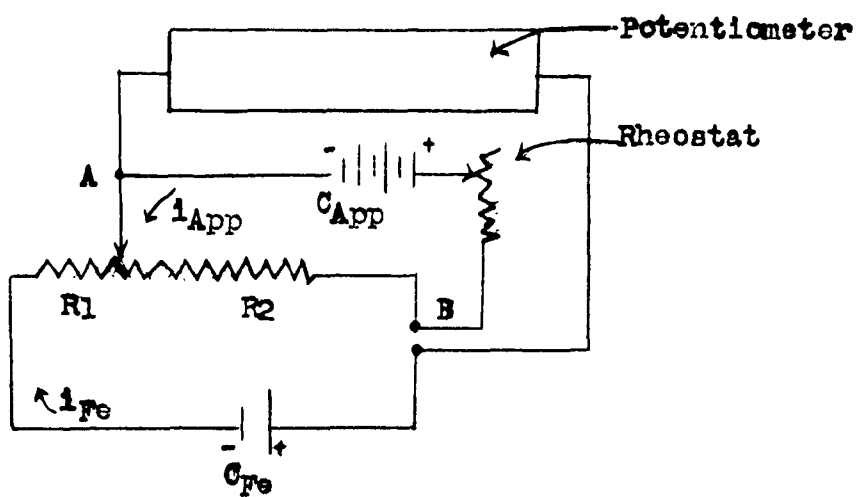
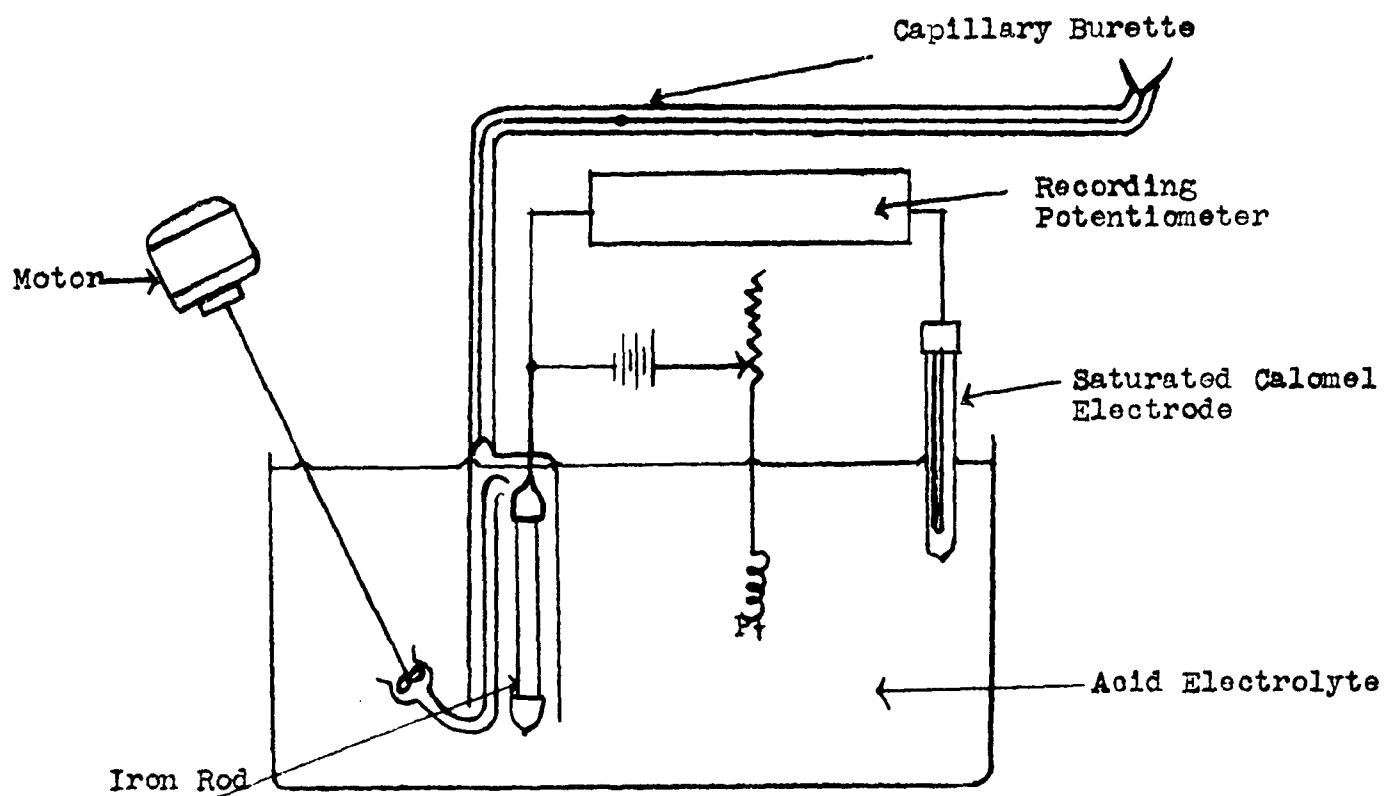


Figure 14



It has been found by the author that reactions of metallic iron are more reproducible when the reactive solution is stirred, provided laminar flow of the liquid over the solid surface is maintained.¹⁹ This is especially true at the extreme ends of polarization curves, and controlled stirring also decreases the concentration polarization²⁰ and hysteresis effects frequently encountered during anodic dissolution.

The hydrogen gas volume was measured at various time intervals by noting the distance that the gas had pushed a drop of mercury of butyl phthalate along a capillary. Joints in the capillary were sealed with mercury rather than grease. At low evolution rates, minute amounts of hydrogen were measured, and therefore, the liquid level in the electrode chamber had to be constant. Because of this, the speed of the circulating motor was maintained by both centrifugal and constant voltage governing. Temperature was held at $25^{\circ} \pm 0.001^{\circ}\text{C}$ by a special thermostat.²¹

Iron dissolved was determined by o-phenanthroline colorimetry.²² Potential was measured by a Sargent recording potentiometer.

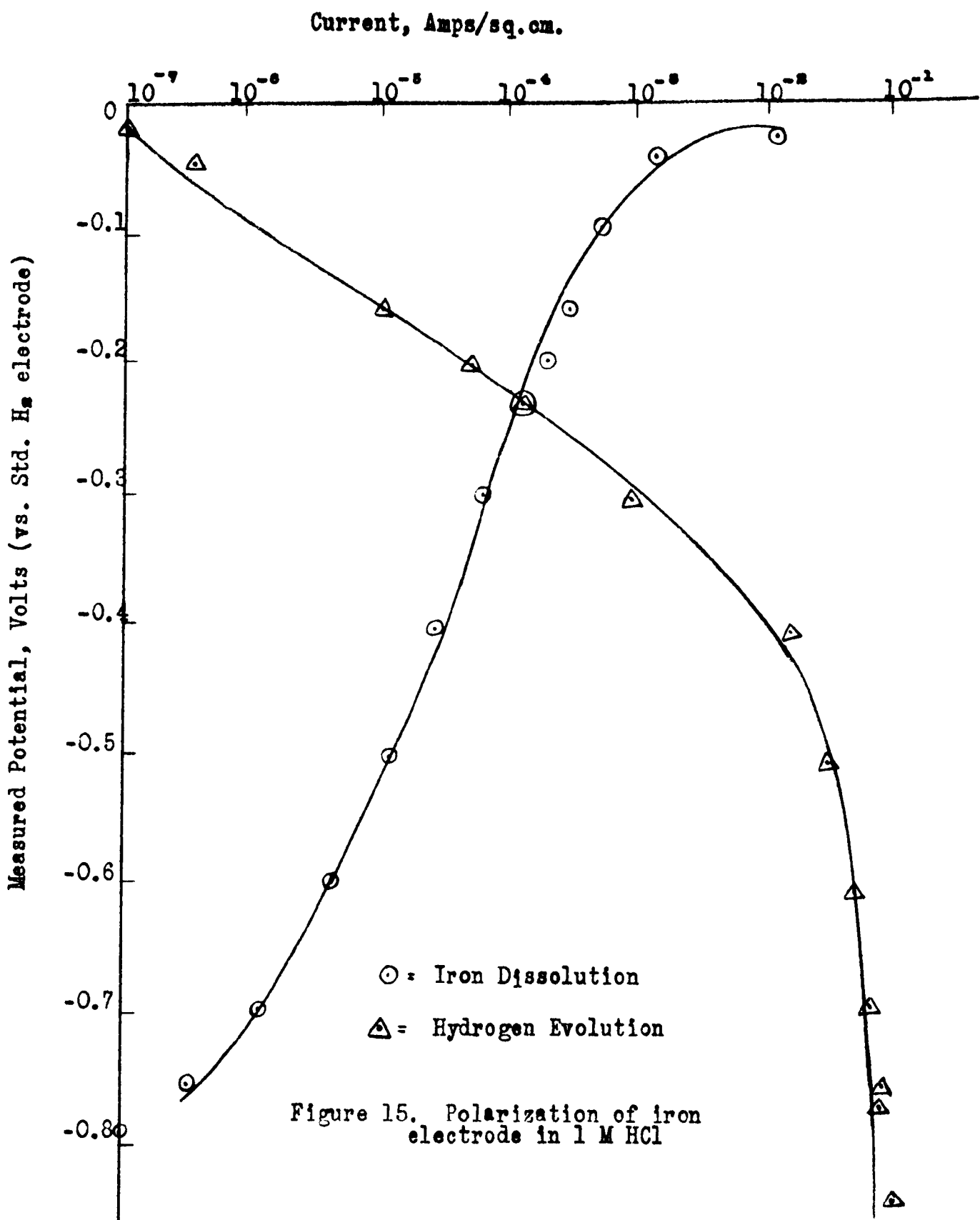
At a given applied current, the apparatus was run until the voltage was constant. Then hydrogen gas and ferrous ion measurements were made at regular time intervals, and both measurements were plotted against time. The reported rates were taken from linear portions of the plots. These reaction rates were always noted at close to three hours from the starting times so that the accumulated ferrous ion was 0.0013 ± 0.0002 molar.

Results and Discussion

In Figure 15 is plotted the results in the form of an Evans polarization diagram.^{15, 88} The circles show rates of iron dissolution, which are the electrolytic currents through the schematic resistance R_1 of Figure 13. The triangles show rates of hydrogen gas production, or the currents through R_2 . Lines through the circles and triangles are the overvoltage curves of iron and hydrogen respectively. The intersection of the curves is the point which describes ordinary corroding iron, with no applied current.

The linear regions of the curves exhibit activation polarization. Since Figure 15 is a semi-log plot, the schematic resistances R_1 and R_2 represent non-ohmic devices. Other types of polarization are exhibited in the high-current regions of the curves.⁸⁰

The current measured is always the net current, that is, dissolution minus plating-out. When the reversible potential of iron is reached, the net current is zero, so this point cannot be represented on a semi-log plot. Near this region, the theory of activation polarization predicts a linear over-voltage plot, and this is extrapolated in Figure 16 to a reversible potential of -0.78 volts for iron dissolution. The ferrous ion concentration was 0.0013 molar, and if the Nernst equation were known to hold for points extrapolated in this manner, an E° of -0.67 volts would be indicated. It is known that the Nernst equation does not hold for iron electrodes under the condition of no applied current. But this anomaly has been accounted for quantitatively by assuming that the Nernst equation does hold for the iron half-cell itself, and that the reaction of hydrogen alters the measured voltage.¹⁵



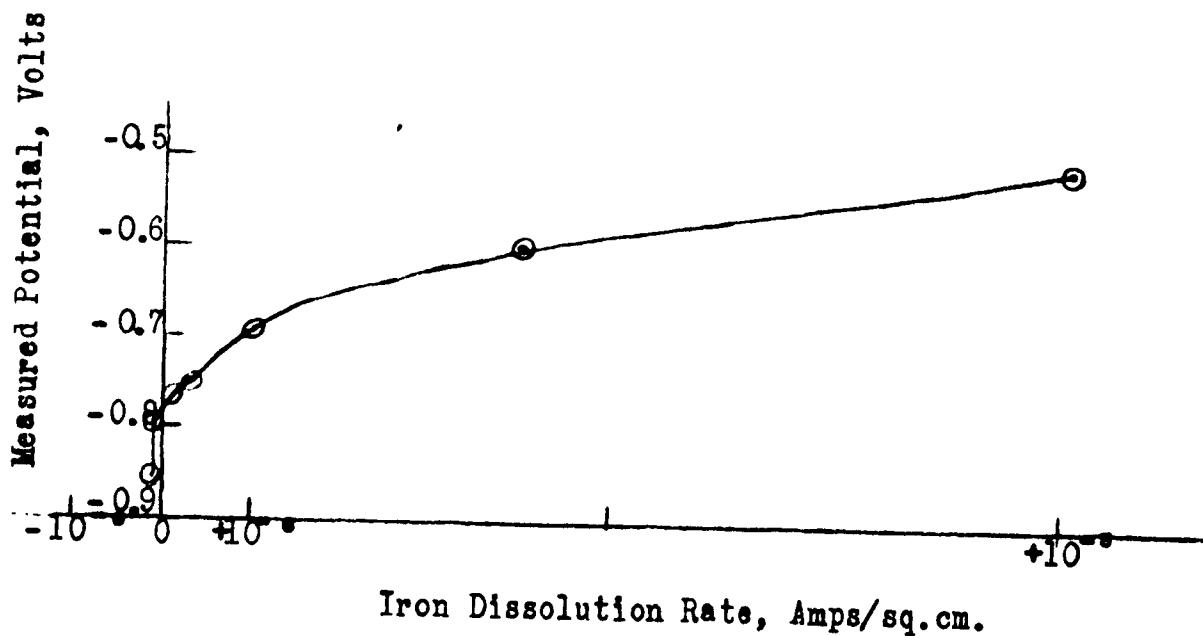
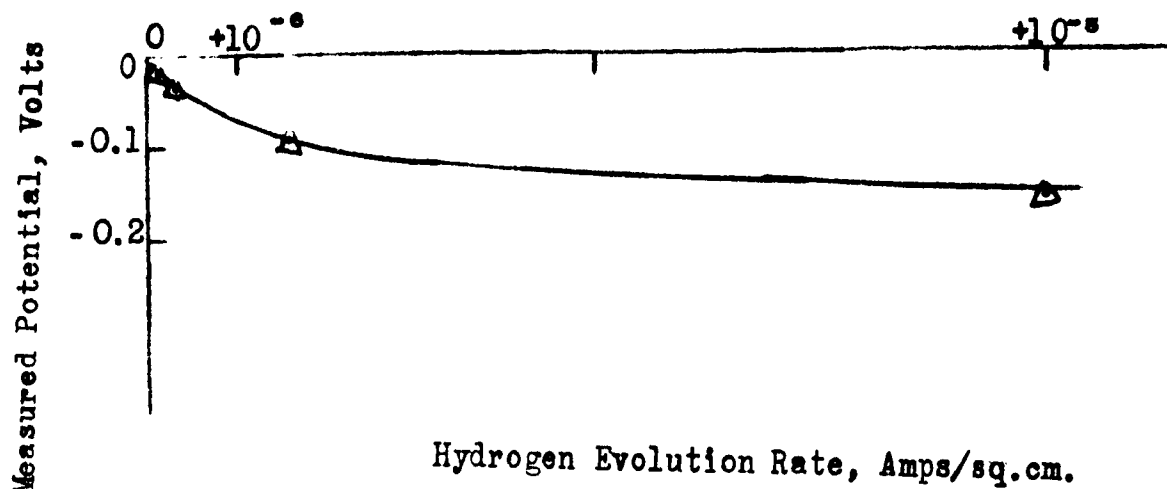


Figure 16.

Low current polarization of iron electrode in 1 M HCl,
linear scale.

The generally-quoted value of E° for iron dissolution in nearly-neutral solution is -0.44 volts.^{16,24} The large discrepancy between this value and the value indicated by the present experiment might be explained by local action currents, which may have been present in the generally-quoted experiments. In the many determinations of the E° of iron dissolution, only the current through the potentiometer was made zero. In those determinations, the current through R_1 , that is, the iron dissolution rate, was not measured. Nor was the Nernst equation tested under exactly those conditions.

Differences between the effective iron surfaces might also explain the large discrepancy. Hydroxyl ion is sometimes able slowly to passivate iron, even in nearly-neutral solutions.²⁵ If this did take place in the generally-quoted experiments, then the true value of E° might be more negative than the -0.44 volts reported.

Similarly, in acid solution, the type of effective surface is likely to be a factor in the present experiment. At the potential necessary to prevent iron from dissolving, the rate of hydrogen evolution is of the order of 0.1 amperes/sq.cm., and therefore a relatively large fraction of the metal surface is likely to be covered with adsorbed hydrogen. The portion of the metal surface which is not covered by hydrogen might have a free energy higher than the free energy averaged over the whole surface. Although this may seem to be a special and unrepresentative case, it might be the only way in which an iron electrode can be made reversible in acidic or neutral solution. Adsorbed layers are also likely to be present on electrodes of other metals, at their reversible potentials, and this is a condition which

is included in the definition of any electrode system.

At the corrosion point, with no applied current, the rates of iron dissolution and hydrogen evolution were both equivalent to 1.26×10^{-4} amperes/sq.cm., and the potential was -0.230 volts. In Figure 13, taking E°_{Fe} to be -0.78 volts, R_1 and R_2 are calculated to be 4400 ohms/sq.cm. and 1800 ohms/sq.cm., respectively, at the corrosion point only.

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C. Testing of the Hypothesis that the Sulfide Ion Acts as A Corrosion Accelerator by Complexing Ferrous Ion.

Sulfur present as sulphite or sulfide ion has been found in this and in other laboratories to accelerate corrosion and hydrogen entry into steel. The action of cyanide and oxalate ions in stimulating corrosion in neutral aqueous solutions has been ascribed to their abilities to form iron complexes. Since there is evidence in the literature that the sulfur-containing anions can form iron complexes in neutral aqueous solutions, it seemed plausible that this was the mechanism by which they stimulated corrosion. This hypothesis was tested in a simple experiment. Two beakers containing flat steel specimens and a large concentration of ferrous chloride in 4.8 N HCl were connected electrically with an ammeter placed in between. A very small amount of sulphite ion was added to one of the beakers and it was observed that the corrosion rate of the specimen in this beaker increased markedly. If complexing occurred in 4.8 N HCl the ferrous ion should have complexed the sulphide ion and the corrosion rate should hardly have been affected.

The cyanide and oxalate ions were also tested in 4.8 N HCl in the absence of ferrous chloride and no corrosion acceleration was observed. A possible explanation is that in very acid solutions these substances do not form stable complexes with iron.

D. Relationship between Electronic Structure and Corrosion Inhibitive Properties.

The relationship between electronic structure and corrosion inhibitive properties was investigated. The apparatus shown in Figure 17 was used. Lowering of voltages indicated inhibition.

Results of a comparison of similar anions are summarized in the following table. Solutions were all made slightly acidic with HCl. Various blanks were run, especially for effects on pH and conductivity.

Table 26

Periodic <u>Group V</u>		Periodic <u>Group VI</u>	
<u>Ion</u>	<u>Inhibitor?</u>	<u>Ion</u>	<u>Inhibitor?</u>
NO_3^-	Yes	-	-
NO_2^-	No	-	-
H_2PO_3^-	No	HSO_3^-	No *
H_2PO_4^-	No	HSO_4^-	No
AsO_3^-	Yes	HSeO_3^-	Yes
H_2AsO_4^-	No	HSeO_4^-	No

* Accelerator

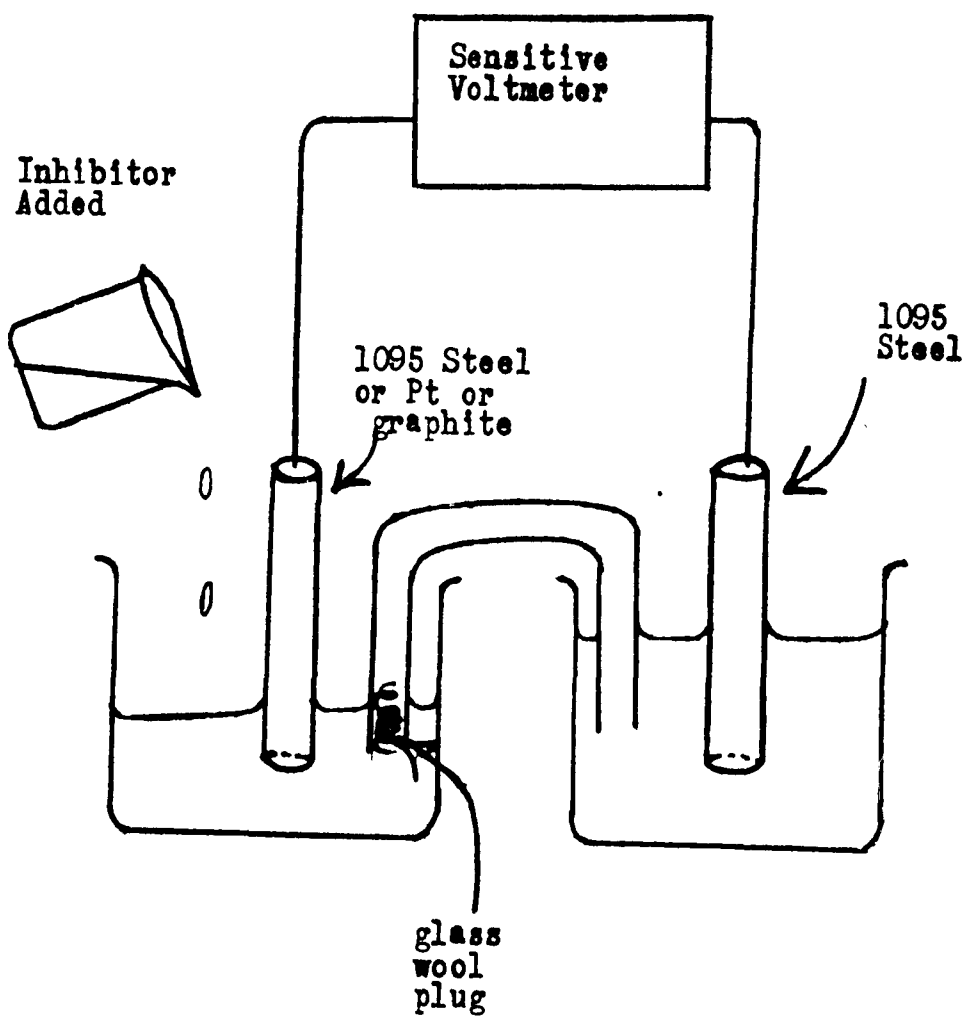


Figure 17. Apparatus for convenient determination of inhibitive properties.

It is apparent from this table, that, except for sulfite, the inhibitors are the ones which have unshared electron pairs. Thus these experiments, along with scattered data in the literature confirm the generally-held opinion that "the presence of an unshared electron pair on the ion is necessary for inhibition."

Presumably, the more easily-donated these electrons are, the better the inhibition. The inhibitor is, of course, competing with water for adsorption sites on the metal. Therefore, the inhibitor must donate electrons more easily than does the oxygen of water. In the table below, it is seen that oxygen holds on to electrons tightly, and therefore, donates them the least.

Also, the table shows that arsenite should be the best inhibitor.

Table 27

Electronegativity Values For Some Elements²⁶

<u>Elements</u>	<u>Values</u>
N	3.0
P	2.1
As	2.0
O	3.5
S	2.5
Se	2.4

 (26) L. Pauling, The Nature of the Chemical Bond, Cornell U. Press
 (1960), page 90.

Thus, theoretical considerations correspond with the facts that (1) these ions are better inhibitors than water, (2) arsenite is an excellent inhibitor and (3) the unshared electron pairs on the

oxygen atoms of the ions are not as important as are the unshared electrons of the central atoms.

Note that phosphite is not an inhibitor, but that this is not anomalous, since the intra-ionic bonding is unusual here, and there is no unshared electron pair.

However, sulfite is an anomaly, since it is an accelerator. Thus, sulfite is the only ion in this series that does not fit the theory. However, sulfite is a well-known catalyst poison, in common with the other ions with unshared electron pairs. It is only in its corrosion behavior that it is anomalous.

With materials that are not anions (see table below), sulfur is also a corrosion accelerating element, in one case. Ammonia also does not fit the theory, since it is not an inhibitor. However, solubility may play a part in the ammonia case.

Table 28

<u>Group V</u>		<u>Group VI</u>	
<u>Ion</u>	<u>Inhibitor?</u>	<u>Ion</u>	<u>Inhibitor?</u>
$\text{NH}_3 \rightarrow \text{NH}_4^+$	No	$\text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+$	-
$\text{NH}_2\text{R} \rightarrow \text{NH}_2\text{R}^+$	Yes*	ROR	No**
		HS	No(Accelerator)
		RSR	Yes(Data from the literature)

* DHQ was the compound used.

** Diethyl ether, saturated solution; also done with alcohol added to make the ether more soluble.

It may be concluded that, with two exceptions (ionic sulfur compounds and ammonia), the unshared electron pair theory fits the facts in three different periods and two different groups of the periodic table, and with both anions and cations. Even sulfur compounds fit, when they are not ionic.

Indications of effect on anodic versus cathodic sites may be noted by considering the direction of potential change when inhibitors are added. The system is extremely simple, and there is little possibility of side effects such as the action of applied voltage on inhibitor itself (since there is no applied voltage).

When both electrodes are steel, no voltage is observed before DHQ is added. Then, when added, DHQ makes its electrode less anodic. Note that the inhibitor causes current to flow between the steel rods where no current flowed before. A comparatively safe conclusion is that DHQ inhibits the anodic areas more than the cathodic areas (See figure 18). (This is in agreement with previously reported corrosion potential data.)

Additional information may be obtained by substituting platinum or graphite for one steel rod in the above apparatus. As in Figure 19, graphite plus Armco iron are similar to a single piece of steel. It was found that the inhibitors and accelerators had no effect on the graphite when added to the graphite (cathode) chamber, but they did reduce the voltage when added to the iron (anode) chamber.

The cathodic areas of 1095 steel are probably not graphite, but are most likely a somewhat metallic material such as iron carbide. Inhibitors might be adsorbed on the actual carbide cathodes, while

Schematic Representation of Apparatus

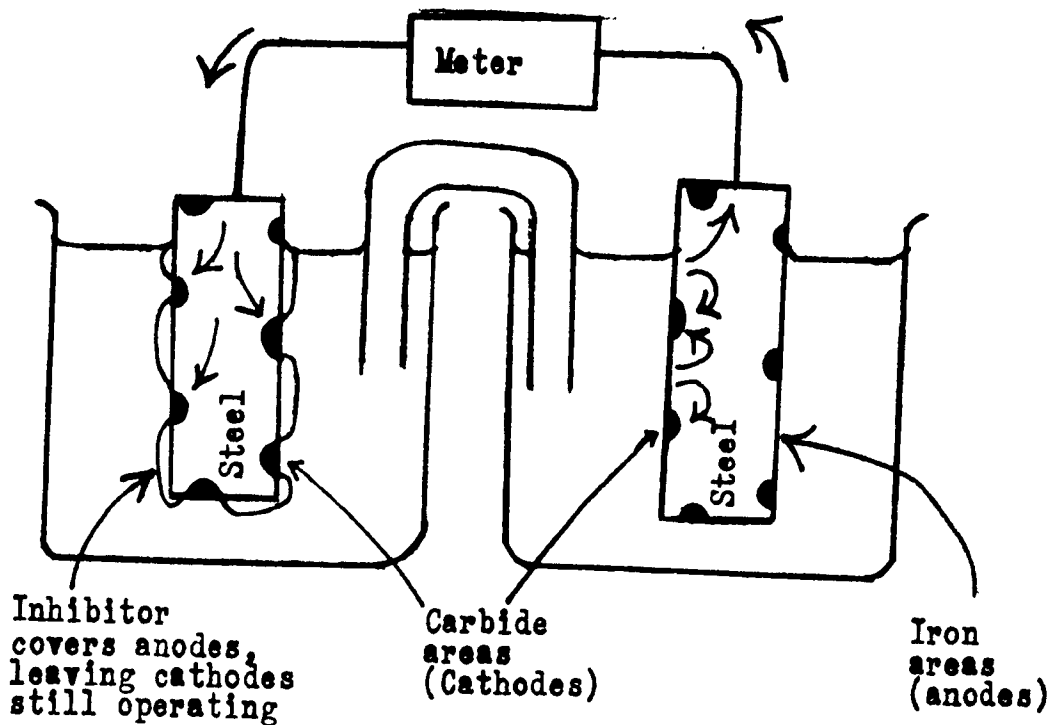


Figure 18

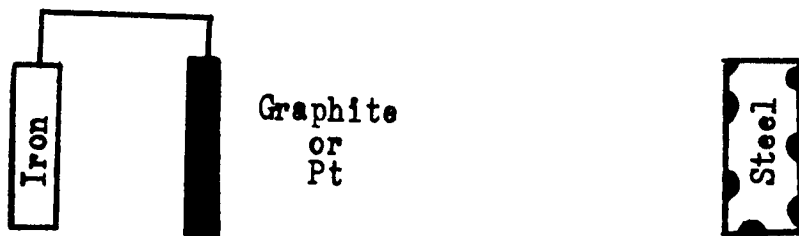


Figure 19

they would not be adsorbed on graphite. However, the inhibitors that adsorb onto carbide should also adsorb onto platinum, since it, too, is a transition metal. When platinum was used as a cathode, all the inhibitors discussed above did decrease the voltage when added to the cathode chamber. This indicates that inhibitors might affect the cathodic areas of steel too. As long as the anodic areas are affected more than the cathodic areas, the voltage should, theoretically, shift the way it actually does.

The conclusion is that inhibitors affect the anodes more than the cathodes of steel but might affect the cathodes somewhat.

The sulfur-containing accelerators had only a very slight effect on the platinum cathode and no effect on the graphite. Thus, their action seems to be specific to iron.

IV.E. Correlation of Moore-Fatigue and "Diffusion Potential" Tests.

Differences in fatigue inhibition by inhibitors have been explained by assuming that these differences are proportional to the amounts of hydrogen diffusing into metal. This assumption has been commonly made by other groups studying the relationship between pickling and the post-pickling mechanical failure.²⁷ To our knowledge

(27) L.D. McGraw et al, NACA Technical Note 2696 (1952).

this has never been proven. The following study indicates that at least for the materials we have studied this assumption is valid within certain limits.

This study was made by comparing fatigue and "diffusion potential" data for several substances. Although in the "diffusion potential"

experiment hydrogen diffusion is not measured, the time-lags are considered direct functions of the hydrogen diffusing into the metal. (At the time this study was made our methods for directly measuring hydrogen diffusion had not been perfected.) The data are plotted in Figure 20.

Considering the level of the reliability of the data it is probably not too rash to consider the deviations of 0.5% hexamine and 0.15% DHQ from the line representing a direct proportion between hydrogen diffusion and fatigue not significant. However, the deviation of the mixture of 0.15% Troeger's Base and 0.5% hexamine does appear to be significant. This is not too serious because the theory presented previously was based upon compounds containing the "formamidine" linkage; Troeger's Base does not.

An objection was raised to the above work because the surfaces of the specimens in the two tests were prepared differently. In the Moore-Fatigue test, the surfaces were machine-ground; the surfaces were etched in the "diffusion potential" test. Unfortunately there was not enough time to check the validity of this objection by testing specimens the surfaces of which are prepared in the same way.

In summary, this brief study indicates that the assumption that differences in fatigue inhibition are due to differences in the amount of hydrogen diffusing into the metal appears to be generally valid. In the mixture in which the deviation from the assumption was significant, neither of the components contained the "formamidine" linkage.

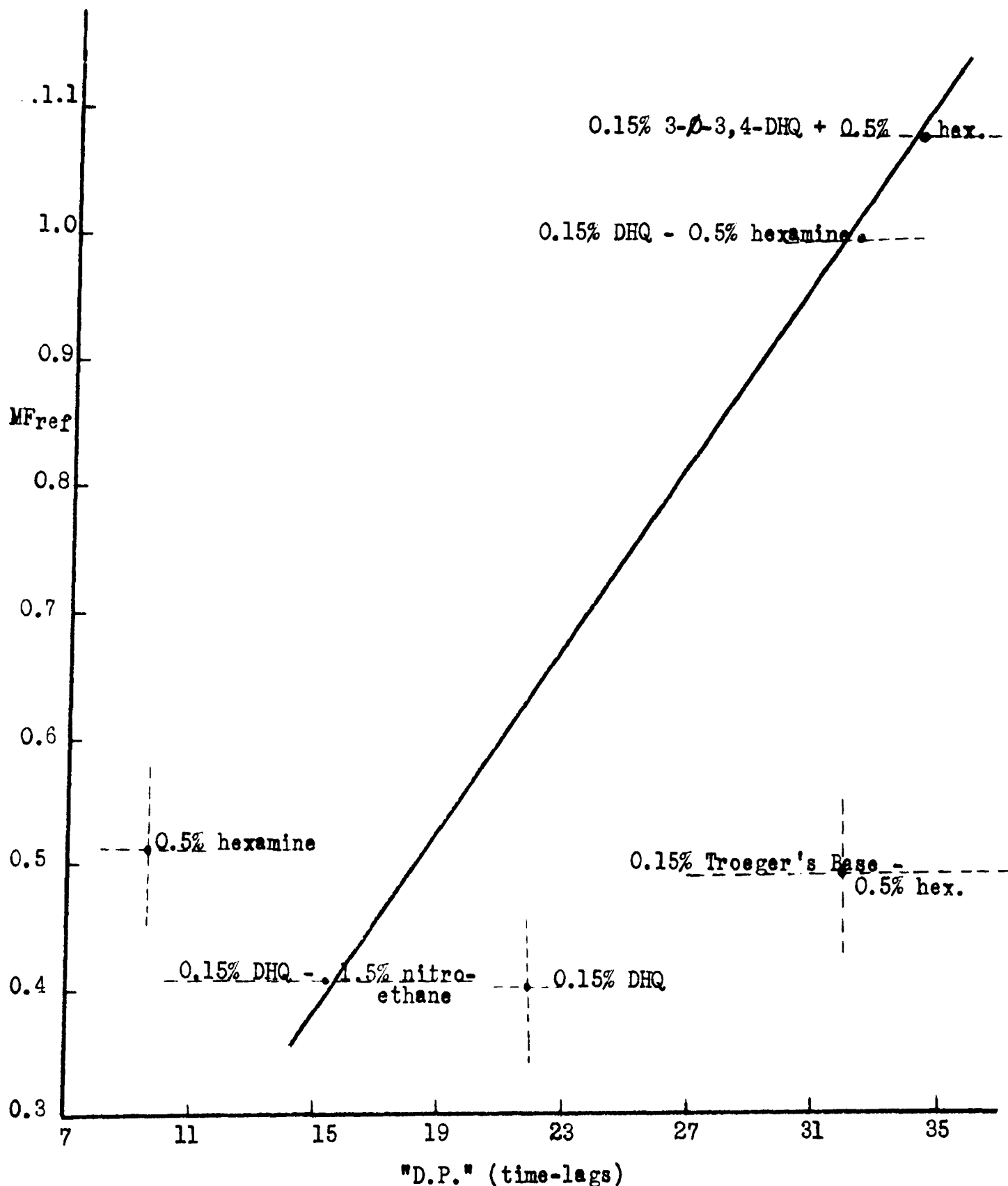


Figure 20. Correlation of "diffusion potential" and Moore-Fatigue data for several substances.
[Dotted lines represent standard deviations.]

V. Tests and Procedures.

A. Moore-Fatigue Tests.

This test which was basic to all our work was, unfortunately, a very difficult one to use. To obtain statistically valid results a large number of specimens had to be tested. The main difficulty appears to be that the steel specimens were not uniform. Other possible sources of error were attacked rigorously - machining, test procedure, etc. Inquiries were made to a leading steel manufacturer about the availability of steel which would be reproducible with respect to Moore-Fatigue testing. We were told that the nature of fatigue was still so obscure that it would be impossible to tailor-make such an order. An effort was made to screen specimens prior to testing by using a non-destructive test, ultrasonic soundings. The time and money consumed in such a testing program was not considered justified in view of the results.

To maximize the possibility of obtaining valid results the following procedure was developed.

Procedure for Breaking Moore-Fatigue Specimens

1. Place a drop of oil into each end of the specimen to lubricate the threads. Also one drop of oil into the tapered end of each spindle. Rotate each spindle to spread the oil. Only a high quality electric motor oil should be used.

2. Insert the specimen into the spindles rotating each to spread the oil uniformly over the area of contact. Push the two spindles together by hand.

3. Insert the two draw bars and tighten as much as possible by hand. Tighten with wrenches until further tightening is very difficult. The draw bar with hollow end is usually used in chuck (spindle No. I.)

4. Place on bed of machine making sure that the trunnions, knife edges, and supporting plates are clean.

5. Connect the hollow draw bar to the rubber bushed coupling by means of the long end of the Allen set screw key.

6. Insert the two retaining pins.

7. Put the loading harness and weight hanger assemblies in place.

8. Have the correct number of weights ready. Place 10 pounds on the hanger and rotate the spindles by hand to ascertain that the sample runs true, i.e., with no wobble.

9. Set the Variac at about 85 volts, see 12 below. Push the black button to start the motor.

10. Add remaining weights quickly but gently.

DO NOT DROP ON HANGER

11. Immediately reset counter to zero.

12. Regulate the speed of the motor to 10,000 r.p.m. The counter registers for each thousand rotations. The Variac settings are normally from 80 to 90 volts for this speed.

13. If there is any undue noise or a noticeable eccentric rotation, something is wrong.

General Procedure for Breaking Specimens from a Single Rod.

1. The source of the samples is a batch of 12-foot, half-inch diameter, cold rolled, annealed rods of 1095 steel. Each of these is termed a rod and will be assigned a number. The rods are cut and machined into blanks which are 3.5 inches long and are faced off and polished on both ends. The blanks are numbered in sequence as they are removed from the rod. A good coat of oil is placed on the ends to prevent rust formation.

2. The word, specimen, will refer to the samples for the Moore-Fatigue Machine after their final machining. The specimens are machined from the blanks. This is now being done by the machine shops of the Rutgers Engineering Department. The center or test section of each specimen was first ground on a coarse grinding wheel to within 10 mils of its final size. A fine grinding wheel was used to bring the minimum diameter to 0.3000 ± 0.003 inch. The specimen is cooled during the grinding process by a stream of liquid.* The test section must not be buffed. The tapers are ground and must fit the taper checking block accurately and with no perceptible wobble.

3. A few blanks from each rod are used to determine whether the rod will be suitable for further use in Moore-Fatigue tests.

4. One or more specimens are broken at a stress which has been found suitable for previous rods from the same batch. The best stress seems to fall in the vicinity of 49-50,000 p.s.i., though the final stress chosen for a particular rod may be a little above or below this range. If the first specimen breaks within the range of $(600-1,000) \times 10^5$ cycles then the second specimen is broken with the same stress. If one is fortunate enough the initial stress used may be the correct * Johnson's TL-131; S.C. Johnson and Son, Racine, Wisconsin.

one for that rod, in which case several breaking points will be obtained with no need to change the stress. The breaking points for these unpickled specimens should all lie within the range, of $(600-1000) \times 10^5$ cycles, and in addition, the range from the lowest to the highest breaking point values should be no greater than 20% of the upper value. The above two requirements must be met by all of the breaking point values at the correct stress and at least four of these values must be obtained. If these two requirements cannot be satisfied, then the rod should be rejected as being unsuitable for further testing. If the first specimen breaks too high or too low, then the stress should be altered in order to bring the breaking point within the correct range. If difficulty is encountered in finding a suitable stress then Dr. Rosenfeld has recommended that at least two specimens be broken at each of two or more different stresses. Then two lines should be drawn, one passing through the points corresponding to the highest breaking value at each stress, and the other passing through the points corresponding to the lowest breaking value at each stress. It is suggested that the correct stress to be tried next is where these two lines meet (provided that this stress is in the required range). If not within this range, discard the rod.

5. Once the stress has been determined at least four specimens should be broken.

6. At least two specimens should be pickled in uninhibited 4.8 N HCl at 37.8 C. for 90 minutes.

B. Shanefield Stirring Apparatus.

During the course of making corrosion studies an apparatus was developed which was simple and gives a high degree of reproducibility. It was developed by one of the participants on this project, Daniel Shanefield, and is designated on this project by his name. The following paper describes the apparatus in detail and the results obtained. It has been submitted for publication in "Corrosion".

"Improved Reproducibility in Corrosion Tests"

Daniel Shanefield, Rutgers - The State University

Abstract - Reproducibility of corrosion tests is frequently poor when strong inhibitors or high carbon steel are involved. Slow, non-turbulent stirring much improves reproducibility, probably by making local convection currents and diffusion more nearly uniform.

Introduction - In the testing of corrosion rates, the reproducibility of experimental results is often so poor that large numbers of runs must be made in order to obtain reasonably consistent and dependable conclusions. The random scatter of results is especially wide when a very effective inhibitor is used and this problem is further aggravated if the tests are made on high carbon steel. In apparatus described here which greatly improved reproducibility in well-inhibited corrosive liquids and also offers some advantage in other cases. The improvement is due to non-turbulent stirring of the corrosive solution.

Special Problems - A statistical explanation for the wide scatter observed in the presence of strong inhibitors is discussed by U. R. Evans.²² It is that, in order for a sample to be truly representative of the larger pool from which it was taken, the sample size must be large. If the sample size is small, then there is a greater likelihood

of chance entering into the results. Very effective inhibitors allow a relatively small number of corroding spots, and thus there is a relatively small sample. This is also true of uninhibited but only weakly corrosive media, where the reaction rate is similarly slow.

In corrosion of high carbon steel, the wide scatter observed is possibly due to the large carbide inclusions and the consequent non-uniformity of specimens. This fairly complex mixture has many parameters which might change from test to test. One of those parameters whose scatter is more apparent in the higher carbon steels is the effective surface area. The area is likely to change because of pitting, and the corrosion rates might, therefore, vary in successive tests.

Design Considerations - In corrosion testing, it seems reasonable that some of the specific causes of statistical scatter are the following:

- (1) differing convection currents of liquid reaction materials and reaction products;
- (2) differing rates of diffusion of materials and products;
- (3) pitting;
- (4) differing distributions of adhering bubbles which protect parts of the metal surface.

It was thought that numbers (1) and (2), that is, convection currents and diffusion, could be made more nearly uniform if an artificially rapid liquid current were imposed in the corrosive solution. Random currents and long distance diffusion would then be small compared to the controlled, uniform flow. The more even distribution of ions might also make less pitting and a more uniform array of bubbles.

Many studies of the effects of solution flow have been made,^{80,81} but the author has found no reference to its effect on reproducibility. Apparatus and Materials - An apparatus for measuring corrosion rates with improved reproducibility is described in Figure 21. The liquid flow itself must be reproducible, and it must be free of random eddy currents near the metal. Therefore, a device for positive measurement of flow rate was incorporated, and the specimen compartment was streamlined.

Paraffin caps were placed over the ends of the steel specimen rods, since it had been found experimentally that the ends of the rods corroded less reproducibly than the sides. The steel rod was 3-1/2" x 1/2". Measurement of the flow rate was accomplished by counting the number of drops passing through the siphon bulb in a given time interval. In all cases, the flow rate was maintained at 6.4 cc. per minute. The centrifugal pump was fabricated from polyethylene sheet, and its top and bottom were a force-fit into the glass tube. (A simple glass propeller-type stirrer, made by pinching the ends of a stirring rod, works almost as well as the centrifugal pump.) The supports for the rod were also made of polyethylene sheet. The siphon was filled by suction through the filler tube. All runs were made in a water bath at 25°C.

The steel rods were cold rolled, spheroidized, S.A.E. type 1095, and the acid was 4.8 N HCl, saturated and de-aerated with hydrogen. A powerful inhibitor, 6-methyl-3-p-tolyl-3,4-dihydroquinazoline,^{81,82} was used in 0.1% concentration.

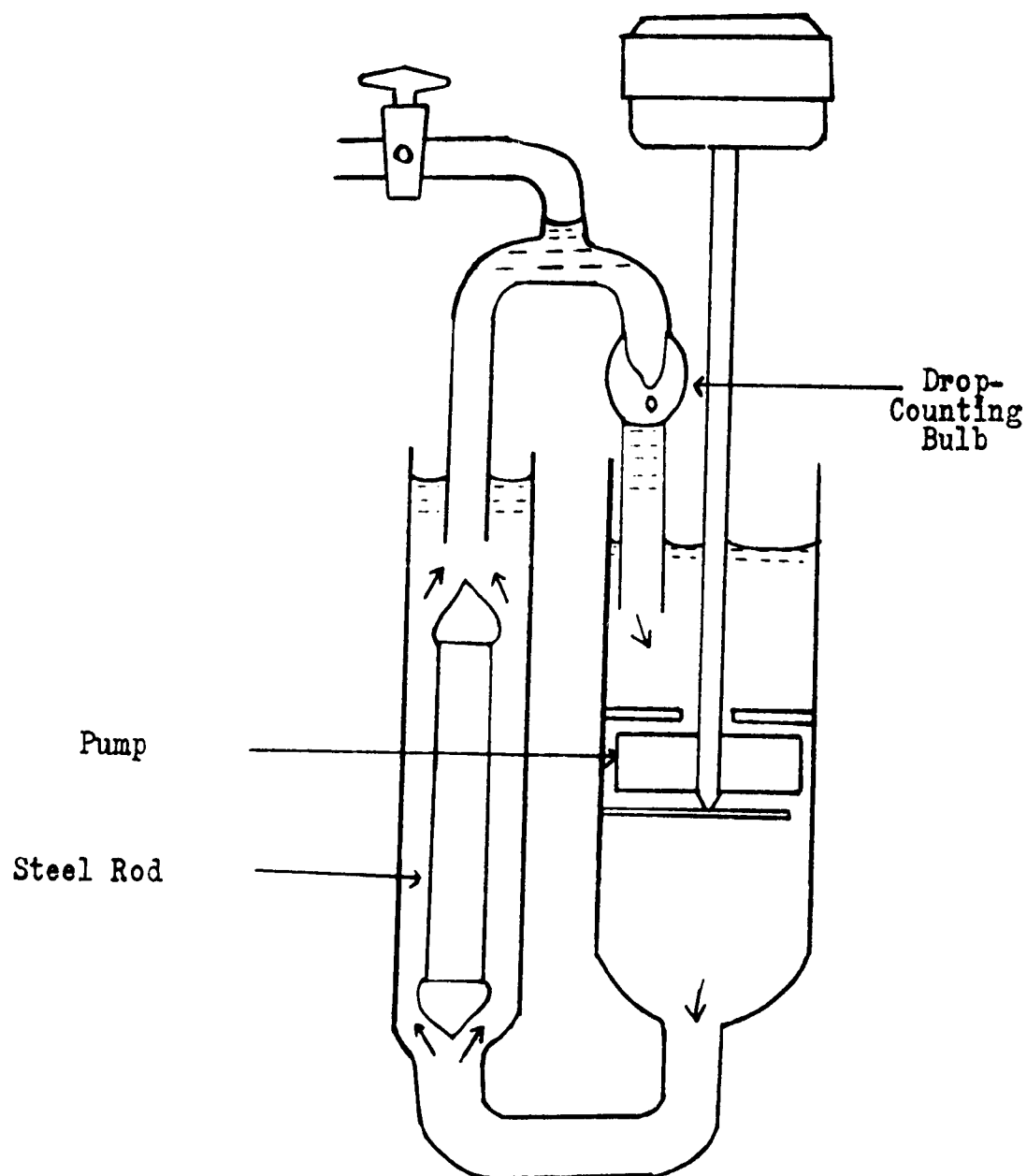


Figure 21. Apparatus for measuring corrosion rates.

Outline of Corrosion Tests - The purpose of the experiments reported here was to get a corrosion rate which would be reproduced when the same steel rod was run again. It could not be expected that different rods would have the same rates. Each experiment consisted of determining corrosion rates three times on each of three rods.

Experimental

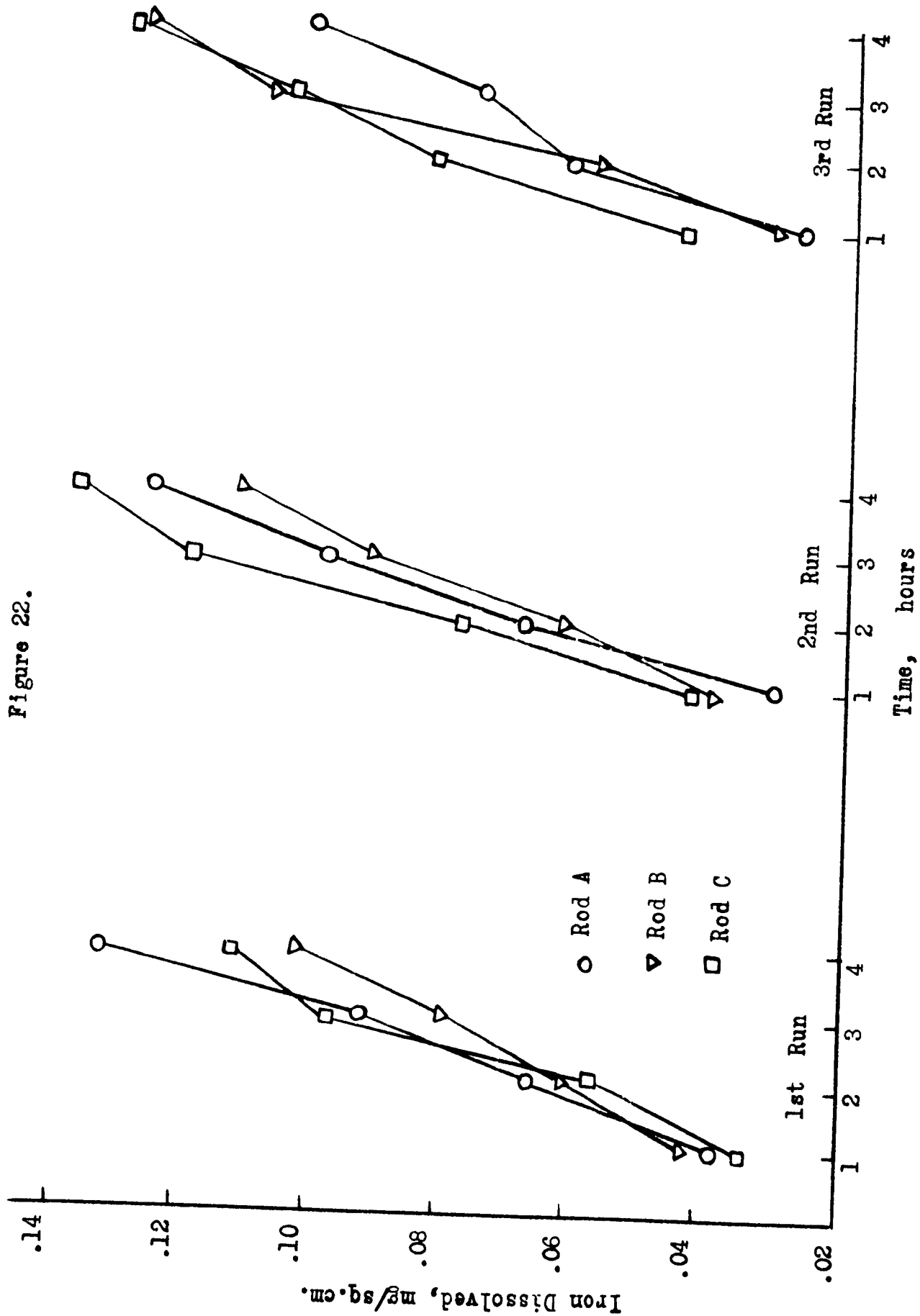
Inhibited Acid - A steel rod, labelled "A", was pickled five minutes in uninhibited 4.8 N HCl to remove oxides and active spots and then rinsed in a stream of methanol. It was air dried and then corroded in the apparatus. Samples were taken every hour and analyzed for iron by the o-phenanthroline spectrophotometric method.³³ In the calculations, corrections were made for the reduction in volume of remaining solution due to the removal of each sample. In the runs without stirring, the stirring motor was operated for five minutes before each hourly sample was taken, to insure that the sample was representative of the whole solution. This stirring period was sufficient to cause two complete circulations of the volume of acid used.

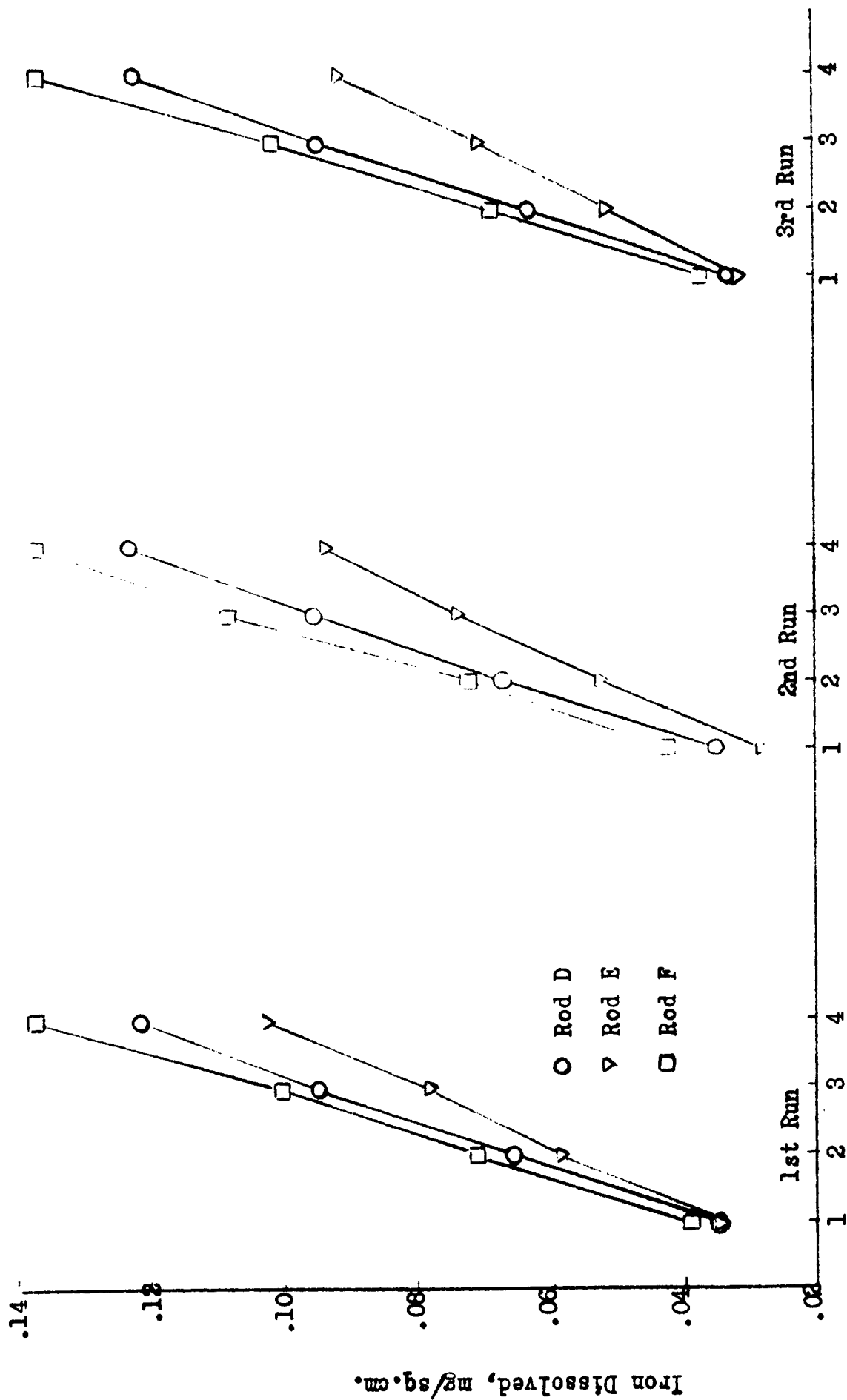
The same rod, rinsed in distilled water and methanol between runs, was run twice more, each time in fresh acid. All inhibited acid samples were taken from the same large batch.

This process was repeated for two other rods, labelled "B" and "C", each one being run three times.

Results are shown for unstirred runs, using inhibited acid, in Figure 22. Corrosion rates, from the best-fitting slopes, are graphed in Figure 24. Reproducibility is very poor.

With the stirring motor operating, three new rods were run, each three times, and the results are shown in Figures 23 and 24. Repro-





Time, hours

Figure 23.

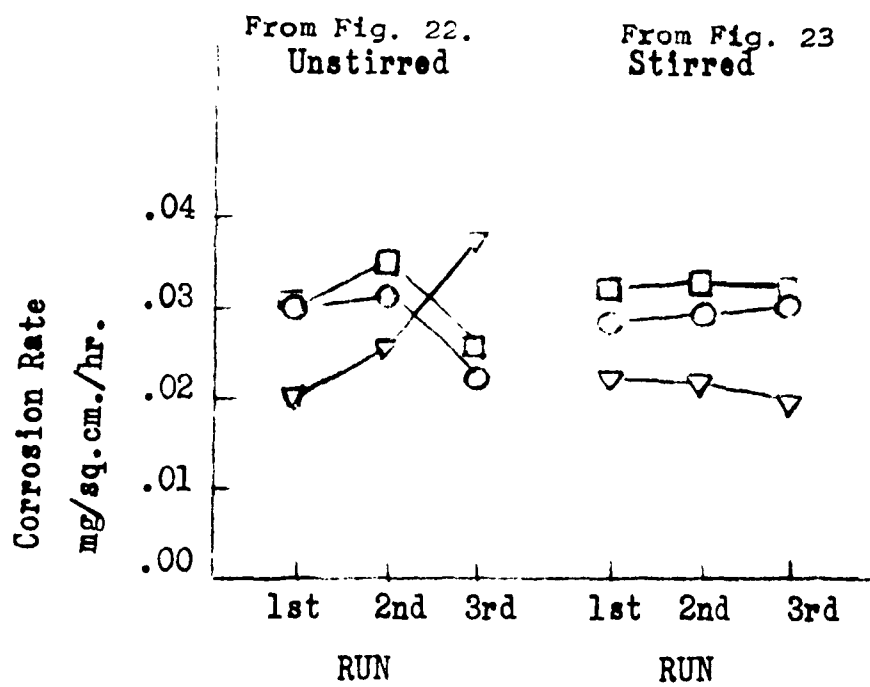


Figure 24.

ducibility is much improved.

Uninhibited Acid - Using uninhibited acid, without stirring, there is not so much scatter. However, as shown in Figures 25 and 27, there is a marked trend toward increasing rates. This increase is probably due to pitting, which should be less severe when small-scale liquid currents are not allowed to stay localized.

As shown in Figure 26 and 27, stirring does lessen the increase in rates. Under microscopic examination, however, differences in pitting were not visible. Pitted metal appeared spongy. Possibly the increases in rates are due to the internal structures of the pits, which were not easily visible with the equipment used.

Bubble Patterns - During stirred runs, bubbles adhering to the metal were observed to be more evenly distributed than during unstirred runs.

Conclusion - Slow, non-turbulent stirring can improve reproducibility of corrosion tests, especially in well-inhibited acid.

Acknowledgments - This work was performed for the U.S. Army under Contract No. DA-30-069-ORD-1680.

The author is indebted to E. R. Allen and P. A. van der Meulen for valuable guidance. Acknowledgment is also due L. Dauerman and R. Eichenbaum for many helpful comments and discussions.

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- (33) W.B. Fortune and M.G.Mellon, Ind.Eng.Chem., Anal.Ed., 10, 60(1938).

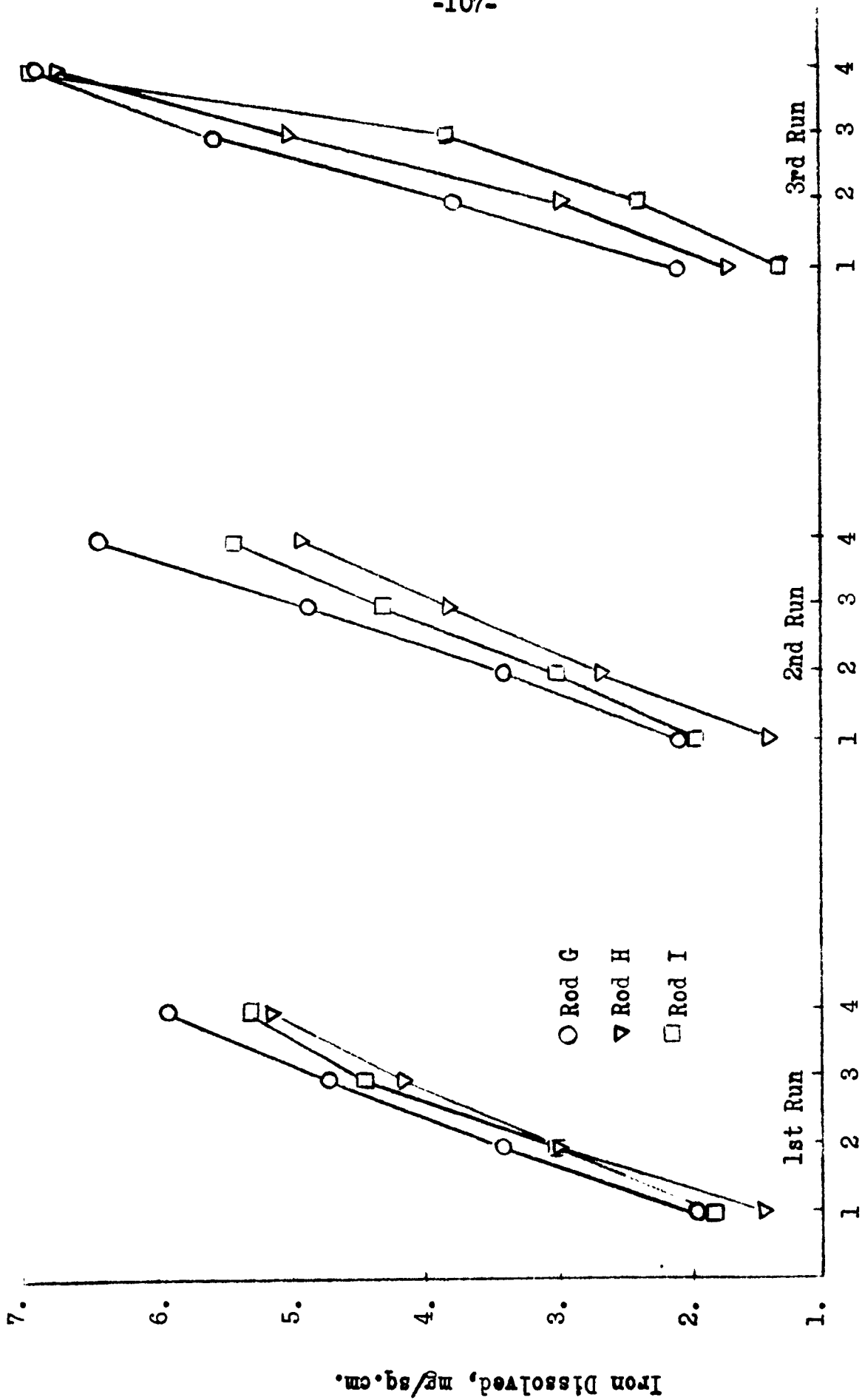


Figure 25.

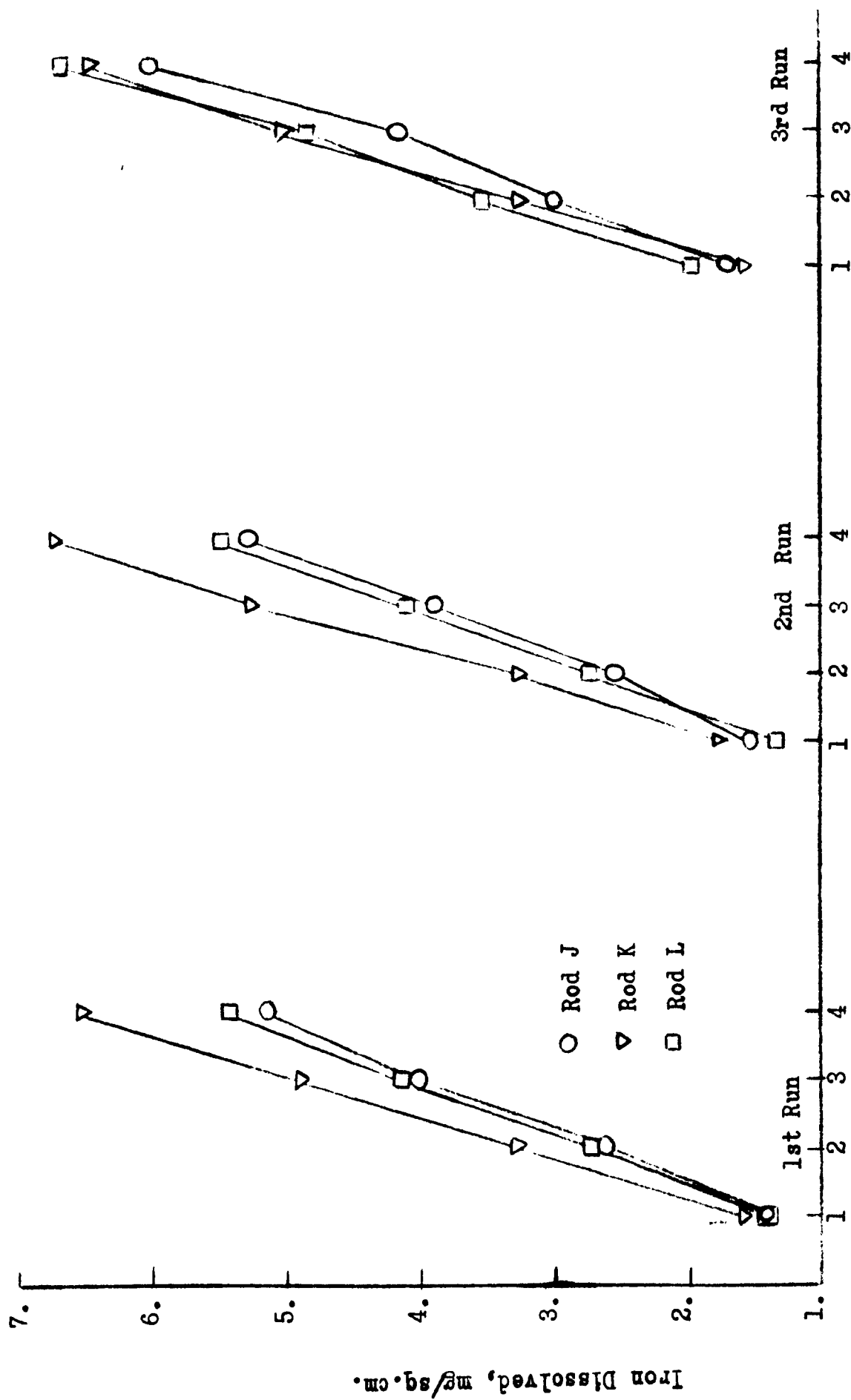


Figure 26.

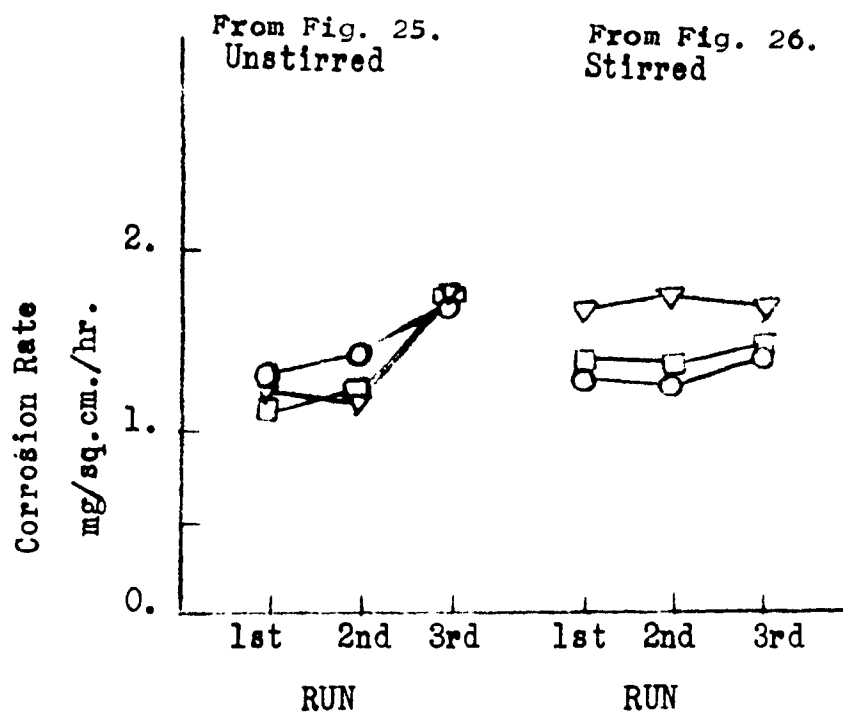


Figure 27.

C. Improved Bath-temperature Regulation.

The following paper has been published in the Rev. of Sci.Inst.
32 211 (1961)

Simple Improved Thermostat System

Daniel Shanefield, Department of Chemistry, Rutgers, The State
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To maintain nearly constant temperatures in refrigerators, water baths, etc., simple on-off systems are ordinarily used. The usual water bath thermostats, in attempts to reach the setting temperatures, overswing by about 0.1°C . above and below the setting. In applications where greater precision is necessary, better than $\pm 0.001^{\circ}\text{C}$ can be achieved by making the heating element current during the cooling period very close to that current during the heating period. However, the regulating power of such a system is easily overwhelmed by large changes in line voltage or room temperature, since the amount of regulation is not sufficient to compensate for large changes.

A continuously variable, proportional system has a minimum of overswing but also has much reserve power in case it is needed. However, such a system usually requires a thermistor and attendant electronic equipment.

A simple on-off system can easily be converted into a proportional system, but without a thermistor as shown in Figure 28. In the manner of usual thermostats, the heating switch oscillates between "heating" and "cooling". This causes the motor to rotate back and forth, but because of the gap in the sector wheel, the crank pin is not moved. To minimize overswing, the cooling resistance is made small,

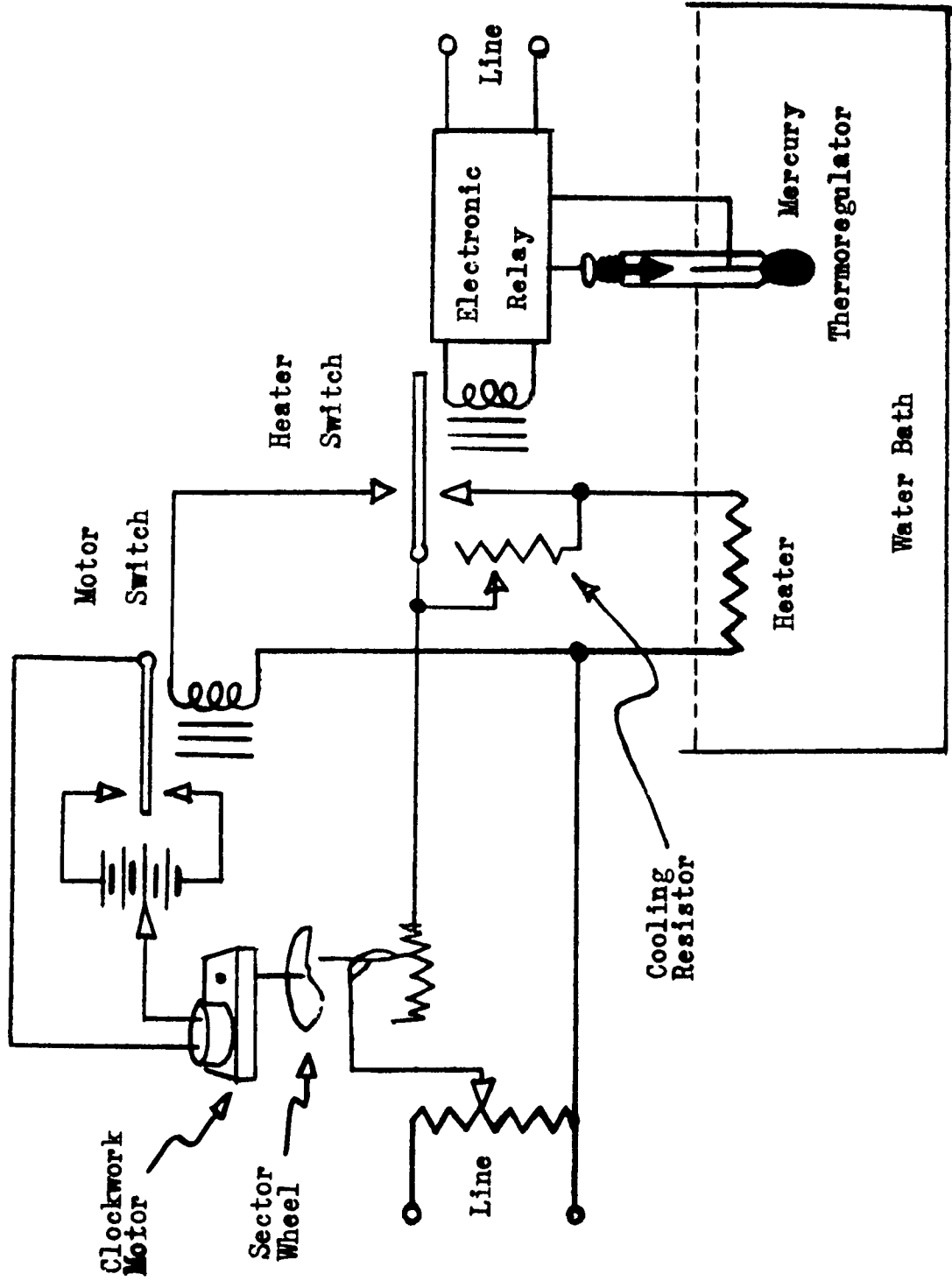


Figure 28.

so that there is little difference between the heating and cooling currents. If a large change in line voltage or room temperature occurs, the heating period will be a longer or shorter time than the cooling period, and the crank pin will then be moved. The voltage will then be changed until equilibrium (equal heating and cooling times) is restored. Long term oscillations and hunting can be damped out by adjustment of the resistances.

The on-off (thermoregulator and switch) sub-system is thus used to replace a thermistor in the proportional (motor-driven resistor) system.

V.D. Colorimetric Method Used for Iron Analyses.

1. Place sample containing 0.01 to 0.12 mg. dissolved Fe into a 25-ml. volumetric flask. The volume of sample should not exceed 9 ml. if the acid content is 4.8 N.

2. Add a volume of 4 N sodium acetate approximately equal to 1-1/2 times the volume of 4.8 N HCl contained in the sample.

3. Add 2.5 ml. of an aqueous solution which is 0.1% in o-phenanthroline, and 1% in hydroxylamine hydrochloride.

4. Dilute to volume with distilled water and mix thoroughly.

5. Measure the transmission of the sample in a 1 cm. cell compared to distilled water as 100%. A Beckman DU spectrophotometer has been used for the transmission measurements at 510 mμ and a slit width of 0.2 mm.

6. The concentration of iron is determined from a calibration curve drawn through transmissions of solutions containing known amounts of Fe.

The Fe content of the distilled water plus 2.5 ml. of the hydroxylamine hydrochloride, o-phenanthroline reagent used in developing the color is less than 0.01 p.p.m. (parts per million). This is negligible in most of the present measurements. Whenever possible all measurements are made within a concentration range of 1.0 to 4.0 p.p.m. Fe. The 4.8 N HCl and 4 N sodium acetate seem to give a larger error. When the larger quantities of 5 ml. HCl and 7.5 ml. sodium acetate were used, .025 p.p.m. of Fe were found. Also DHQ and related compounds show a small interference in the concentrations used in the pickling baths. The maximum obtained with the largest concentration and volume of DHQ used is .04 p.p.m. Fe. The hexamine used shows a smaller error. The appropriate blanks will be run with each set of samples in the future and the resulting corrections subtracted from the p.p.m. Fe found. When standards are measured a very good Beer's Law plot was obtained from 10 to 100% transmission. A straight line agrees with the experimental points so well that the results are now being calculated on the slide rule using a value of 2.5 p.p.m. Fe at a transmission of 32.0%.

V.E. Hydrogen Diffusion.

The basic procedure has been described by Davis and Butler.³⁴

 (34) R.T. Davis, Jr., and T.J. Butler, J. of Electrochem. Soc., 105,
 563 (1958).

The modifications described below were made to cope with our particular problems.

In the initial stages of our diffusion study, changes in potential were used as the criteria for comparing the activities of

the various substances. It became apparent as more data accumulated that the time-lag between the addition of acid to the cell and the observation of a change in the steel-chromate potential was a more reliable measure. As in the case of the total potential change, the time-lag seemed to depend on the initial passive potential but to a much lesser extent. Still it was of sufficient magnitude to necessitate studies to make the passive potentials constant.

Various methods were tried in order to obtain constant initial passive potentials.

(a) Short-circuiting. The calomel electrode was connected directly to the steel sheet for various lengths of time and then disconnected. Repeating this process caused each cell's potential to reach a constant value. However, the constant potential of one cell would not be the same as that of another cell, so this method was abandoned.

(b) Anodizing. The metal plate was made an anode in an electrolytic cell. As can be seen in Table 30, various current densities and total coulomb values were tried. Area was fixed.

Table 30

<u>Current</u>	<u>Time</u>	<u>Resulting Potential, mv.</u>				
		<u>Cell A</u>	<u>Cell B</u>	<u>Cell C</u>	<u>Cell D</u>	
50 ma.	1 hr.	415	460	450	---	Potentials varied with time
50 ma.	2 hrs.	420	450	448	---	Potentials constant with time
25 ma.	2 hrs.	290	487	492	435	Potentials varied with time

Constant passive potentials of 435 mv \pm 15 mv were found for a 50 ma. current applied for 2 hours.

The reproducibility of the time-lags increased with the use of cells having a constant initial passive potential but still left much to be desired. It was found necessary to pickle the sheets several times and to use a comparison blank to increase the reproducibility. The comparison blank procedure is based upon data in Table 31.

Table 31

<u>Sheet No.</u>	<u>Time-lag After 1st Acid Attack</u>	<u>Time-lag After 2nd Acid Attack</u>	<u>Time-lag After 3rd Acid Attack</u>	<u>Time-lag After 4th Acid Attack</u>
1	11 minutes	8	7	11
2	16 minutes	---*	---	---
3	7 minutes	---*	---	---
4	11 minutes	8	6	12

Sheets No. 1 and No. 4, which have approximately the same time-lag after the first acid attack, have approximately the same time-lags after subsequent attacks. This means that one sheet can be used for a blank run while the other is used to test an inhibitor. The blank is necessary, since the permeability of the sheets seems to change from run to run.

* Sheets Nos. 2 and 3 were discarded because their time-lags after the 1st acid attack were unequal.

V.F. Determination of pKa.

The method⁸⁸ of determining the pKa values consists of dissolving

 (35) Elderfield et. al., J.Org.Chem., p. 405 (1947).

the substance under investigation in 50% aqueous-alcohol and determining the pH with a Beckman pH meter at the half-neutralization point. At this point $pH=pK_a$.

VI. Chemical and Physical Analyses of Specimens Used.

Some of the steel specimens used in this investigation were subjected to chemical and physical analyses at Aberdeen Proving Ground. The following results were obtained.

Table 32

Experiments in which Samples
were used.

<u>Sample</u>	<u>Use</u>
A - D (spring steel)	1) Corrosion measurements 2) Diffusion potential
E, F	Moore-Fatigue experiments
G, H	Hydrogen evolution experiments
I, K	Corrosion potential experiment
J	Diffusion potential experiments

Table 33A. Chemical Analysis.

<u>Sample</u>	<u>Carbon</u>	<u>Manganese</u>	<u>Sulfur</u>	<u>Phosphorus</u>	<u>Silicon</u>
A-Plate	.97	.38	.031	.018	.20
B-Plate	.91	.38	.033	.014	.20
C-Plate	.91	.39	.038	.011	.22
D-Plate	.97	.38	.027	.013	.20
E-Machined Specimen	.96	.39	.034	.010	.20
F-Machined Specimen	.95	.38	.035	.011	.22
G-Rod	.93	.34	.029	.010	.23
H-Rod	.92	.34	.031	.011	.23
I-Rod (Short)	.91	.39	.029	.012	.19
J-Sheet	.95	.41*	---	.016*	---
K-Rod (Short)	.81	.39	.02***	.010	.20

B. Metallurgical Examination.Test Procedure -

1. Longitudinal, transverse and surface sections from the plates and longitudinal and transverse sections from the bars were mounted and polished for microscopic examination.

2. Photomicrographs were taken at 500 X showing variations in Fe_3C particle size and distribution.

3. The hardness of one sample from each of the three groups was taken using the Tukon microhardness tester, 500 gm. load.

*Not run because of insufficient sample.

* * Sample did not dissolve as fast as required.

Test Results -

1. Metallurgical examination revealed that all eleven samples had received a spheroidizing treatment.

2. The most noticeable difference was Fe_3C particle size and distribution, (Ref. Figure 29). Based on this difference the specimens may be classified in three groups as follows:

a. Flat plates (A, B, C, D, J): Fairly uniform spheroidized structure with relatively large Fe_3C spheroids.

b. Round stock (G, H, I, K): Partially spheroidized structure showing slight evidence of prior pearlite lamellae. Finer spheroid size than plate samples.

c. Fatigue specimens (E, F): Spheroidized pearlitic-type structure with very fine Fe_3C spheroids. Pearlite lamellae very evident.

3. The inclusion content ranged from ASTM A-1 (thin) to A-3, B-2 (thin). In general the steel appeared moderately clean although one of the fatigue specimens (F) contained a fairly high sulfide and oxide count.

4. The results of the hardness test were as follows:

<u>Sample</u>	<u>Table 34</u>	
	<u>Hardness of Samples</u>	
	<u>Knoop</u>	<u>conv. to Rockwell</u>
Flat Plate (spec.D)	187	86 RB
	187	86 RB
	185	86 RB
	183	85 RB
Round Stock (spec.H)	274	24 RC
	261	22 RC
	264	22 RC
	271	23 RC
Fatigue Specimen (spec.E)	271	23 RC
	264	22 RC
	255	20 RC
	271	23 RC

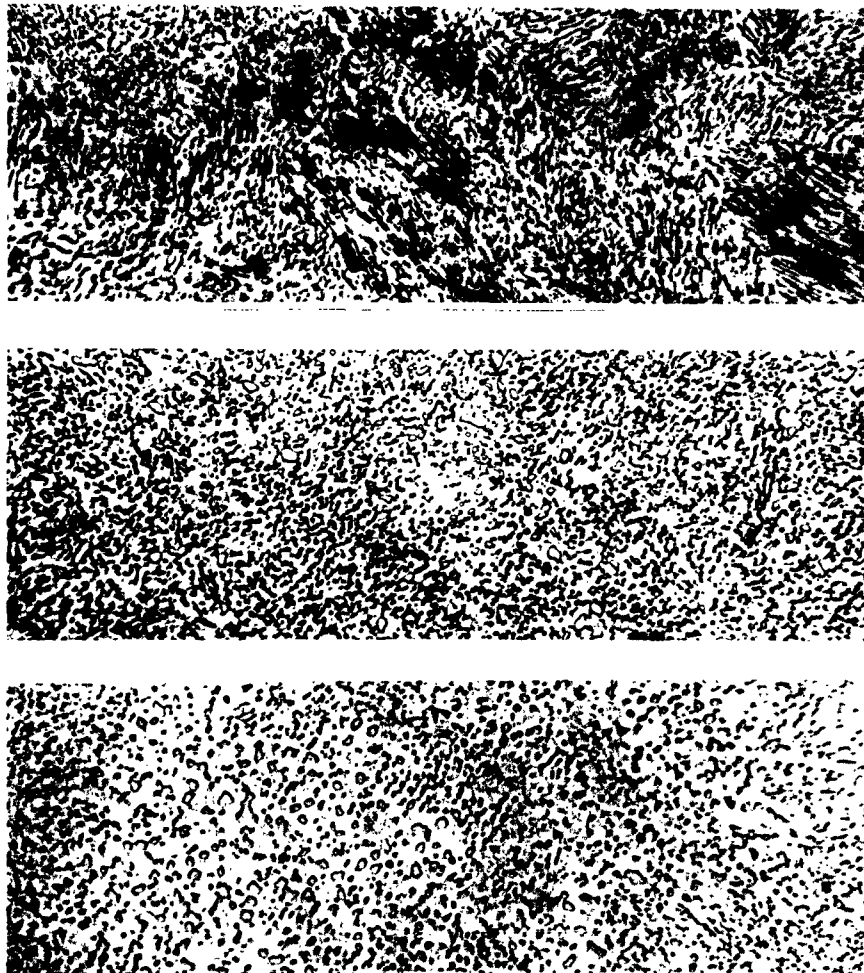


Figure 29 500 X
Representative sample from each group
showing variation in Fe_3C particle size
and distribution. Top-specimen D, center-
specimen H, bottom-specimen E.

Discussion -

1. Metallurgical examination of the eleven samples revealed a variation in microstructure.

2. Spheroidization of carbide is accomplished by heating at a temperature just below the critical range for a long period of time.

3. The differences in Fe_3C particle size and distribution in the samples examined may have been caused by a number of variables which affect spheroidization. Increased time at temperature, finer initial carbide and prior cold working all favor spheroidization. Although all except flat plates were made from the same heat of steel it is probable that due to the temperature gradient during cooling, differences in initial carbide size did exist. The plate samples had received the most cold work and had been more completely spheroidized than the other samples. Evidence of pearlite lamellae in the fatigue specimens indicates insufficient time at temperature for the carbides to spheroidize.

4. The more completely spheroidized the carbide in a material of this type the lower the tensile strength, yield strength and hardness

5. The effect of the difference in microstructure on the tests being conducted by the Coating and Chemical Laboratory is beyond the scope of this examination.

VII. Future Work

A. Studies directly related to the purpose of the original project.

1. Testing of Theory.

a. Determination of ratio of Hydrogen evolved/Hydrogen diffused into metal.

If the theory is valid, this ratio for a formamidine-type inhibitor should be larger than when no inhibitor is present and in a series of formamidines it should increase with the pKa of the formamidine.

b. Evaluation of 3-cyclohexyl DHQ.

This compound should be synthesized in higher yields than previously. Its pKa should be measured and if, as predicted, it is considerably higher than the pKa of any of the other formamidines tested previously, a mixture with hexamine should be evaluated. It had been predicted from the theory that such a mixture should be a better embrittlement inhibitor than has previously been tested.

2. Significance of size in the effectiveness of formaldehyde.

It appears that formaldehyde is effective in the presence of DHQ because of its small size. If this is the case, larger aldehydes should be less effective. Such a series of mixtures should be tested.

3. Corrosion Potentials and Adsorption.

It had been observed that the corrosion potential of a mixture of DHQ and hexamine is equal to that of the sum of the potential of these substances taken singly. A possible explanation is that DHQ and hexamine are adsorbed independently. This is only speculative

because the relationship between the corrosion potential and adsorption has not been studied. Such a study would be important not only for explaining the DHQ-hexamine result but in general. This work might lead to a simple method for measuring adsorption.

4. Agreement between Diffusion Potential and Moore-Fatigue.

Determine if a greater degree of agreement can be obtained when the method of preparing the surfaces of the specimens are the same.

B. Basic Related Studies.

1. Determination of factors contributing to hydrogen embrittlement resulting from pickling.

In comparing the Moore-Fatigue results for various inhibitors it is difficult to interpret the data because the factors contributing to fatigue strength loss under pickling conditions have not been completely determined. The most likely cause for the M-F difference is the diffusion of different amounts of hydrogen into the steel. But it was pointed out previously that the changes in fatigue strength do not agree completely with the amount of hydrogen diffusing into the steel. Other factors are involved. A similar situation arose in another large-scale study of the effectiveness of pickling inhibitors in preventing hydrogen embrittlement as measured by a bend test. This study was conducted at Batelle Institute.⁸⁷ Although the investigators interpreted their bend test data in terms of the effectiveness of a substance preventing hydrogen diffusion, they also observed no correlation between the amount of hydrogen in the metal and the bend test result.

It seems clear that in order to obtain a fundamental understanding of mechanical embrittlement inhibition, it is necessary to determine the factors which cause the embrittlement.

2. Heat of adsorption of inhibitors from Solution.

The activity of many organic corrosion inhibitors has been explained by their ability to be chemisorbed on the metals that they protect. Chemisorption implies that the bond strength between the metal and the inhibitor is approximately greater than 10 kcal./moles or greater. But thermodynamic data have not been gathered as yet to support this explanation.

The solution of this problem can be divided into three successive stages of increasing complexity. The first is a study of the relationship between the inhibitor and the metal. Following this, a study of the effect of adding a solvent can be made. The final stage will be designed to permit the study of the effect on corrosion.

The relationship between the inhibitor and the metal can be studied by determining the heat of wetting by a liquid inhibitor like ethyl sulfide which has been assumed to be chemisorbed on metals of the transition series. From this information and the total surface area of the metal, which can be determined by the BET method, it should be possible to decide whether chemisorption has occurred.

Other information of importance can be obtained from this type of experiment. It is often stated that chemisorption will take place only on metals containing available d orbitals. This can be tested by comparing the activity of the inhibitor on zinc and platinum. Another application will be in attempting to explain why corrosion

inhibition increases with basicity in a series like the ammonia-trimethylamine one. The usual explanation is that the more basic (Lewis base) substances are capable of forming stronger bonds with the metal. On the other hand, since the degree of adsorption and presumably the degree of corrosion inhibition depends on the difference between the solvent-affinity metal-affinity of the inhibitor it seems unfair in the absence of data to ignore the former factor in favor of the latter. Using the method described above the metal-affinity can be determined exclusively. This particular series can be studied only with great difficulty because of the low temperatures needed to liquify these amines. However, other series can be found which are liquids at room temperature. It is suspected, however, that the controlling factor may vary with the series and that every effort should be made to study the above-mentioned amine series afterwards.

The problem becomes considerably more complicated when a solvent is present. To determine the effect of the solvent, organic or inorganic more experimental data will be needed. In addition to the heat of wetting by the inhibitor the following additional information will be needed:

- a. The heat of wetting by the solvent.
- b. The heat of solution of the solvent and the inhibitor.
- c. The heat evolved when the inhibitor is added to a mixture of the metal and the solvent.
- d. The amount of inhibitor adsorbed.

Proper interpretation of these data should yield the heat of adsorption of the inhibitor.

The final stage brings in one further complication--corrosion. The complications increase arithmetically but the experimental problems exponentially. The evolved heat measured when a corrodible metal is added to a solvent-inhibitor solution is a hybrid composed of many thermal effects: heat of reaction, heat of adsorption of the solvent, heat of adsorption of the inhibitor, and probably other factors. In addition, this system is dynamic and is, therefore, constantly changing. Under these conditions it does not seem possible to determine the heat of adsorption of the inhibitor. Instead of attacking the problem head-on an indirect scheme is proposed.

We want to determine the enthalpy for the process in which the inhibitor is adsorbed on the sites made available during corrosion. The enthalpy of the process in the reverse direction must be the same as that for the forward one except that the signs are reversed. It appears that the reverse process is more amenable to study because the thermodynamic measurements would be made in situations similar to stage 2. First the metal in powder form will be placed in an acidic solution containing the inhibitor. No measurements will be made. The powder will then be placed in an organic solvent that has a considerable higher heat of wetting than the inhibitor. The inhibitor will, therefore, be displaced from the metal. The heat of wetting of the metal will be diminished by a factor which corresponds to the heat of adsorption of the inhibitor from the solvent. If the heat of solution of the inhibitor in the solvent is also determined then it should be possible to calculate the enthalpy for the process,

(a) inhibitor (liquid state) \longrightarrow inhibitor (corroded metal).

The enthalpy for the process,

(b) inhibitor (acid solution) \longrightarrow inhibitor (corroded metal).

can be calculated by measuring the heat solution of the inhibitor in acid solution and subtracting this value from the first value obtained.

3. A proposed test for determining whether an inhibitor is chemisorbed on a corroding metal.

Information concerning chemisorption is important in elucidating corrosion inhibition mechanisms. It is difficult to establish whether an inhibitor is chemisorbed onto a corroding metal without disturbing the system by removing the metal. Calorimetric procedures are complicated because factors such as the heat of adsorption of the solvent, the heat of the acid-metal reaction, and the heat of solution of the substances must be taken into account. The following proposed method it is believed might be simpler; however, it will probably apply only to resonance-stabilized organic substances which are not reduced. Many of the compounds we have studied are of this type, e.g., DHQ.

The proposed method is based on the observation that resonance-stabilized organic molecules, like benzene, in the gas phase can be chemisorbed on transition metals and when this occurs in the presence of deuterium more rapid deuterium exchange occurs than otherwise. Thus a criteria for gas-phase chemisorption of a resonance stabilized organic molecule is the deuterium-exchange rate. In deuterium rich acid solutions, if the situations are analogous, metal-acid attack should result in more rapid deuterium exchange when a substance is

chemisorbed than otherwise. The bulk of the available evidence indicates that substances of the type under consideration will be chemisorbed on a transition metal and not on a non-transition one, e.g., sodium amalgam. It is predicted that if a substance is studied which does not chemisorb easily, e.g., cyclohexane, the deuterium exchange rate will not depend on the metal used; however, if the substance can be chemisorbed, the rate of deuterium-exchange should be greater when a transition metal is used.

Actually this method might be more applicable than is now thought. It is possible that in general the chemisorbed organic molecule undergo a more rapid deuterium exchange rate than otherwise.

A reference of interest in this study is by E.B. Maxted and M. Josephs³⁰ which indicates that when thiophene is chemisorbed on

(36) E.B.Maxted and M.Josephs, J.Chem.Soc., 2635 (1956).

platinum it loses its resonance energy.

4. Determination of E°_{Fe} .

This is a continuation of the study previously discussed. The problem is to calculate the E°_{Fe} from data which are not derived from electrode potential measurements of iron in an aqueous solution.

5. Determine effectiveness of substances directly reduced by atomic hydrogen as hydrogen embrittlement inhibitors.

The "diffusion potential" studies on H_2O_2 were promising. In conjunction with a good corrosion inhibitor like DHQ, assuming no chemical interaction occurs, a truly superior hydrogen embrittlement inhibitor might be obtained.

6. Testing of Hypotheses to Explain the Superiority of HCl to comparable concentrations of H_2SO_4 with respect to preventing hydrogen embrittlement.

It is generally accepted that corrosion in HCl causes less embrittlement than in a comparable concentration of H_2SO_4 . It also has been reported that the ratio of Hydrogen evolved/Hydrogen diffused into metal is greater for HCl than H_2SO_4 .⁸⁷

(37) S.A. Balezin and D.Ya.Solovei, Doklady Akademii Nauk, SSSR, 75, 811-814 (1951).

One possible reason, in line with the Rosenfeld theory, is that the chloride ion is adsorbed more extensively on the anodic than the cathodic areas of metal. Another possible cause is that sulfites are present in H_2SO_4 and these act as hydrogen diffusion accelerators. Both of the hypotheses should be amenable to experimentation.

7. A study of the Mechanism by which Sulfur accelerates Corrosion.

The formation of a stable ferrous complex was shown to be unlikely. This result suggests that the acceleration is not due to a thermodynamic cause but to a kinetic one. A possible kinetic reason is that a ferrous ion-sulfur activation complex forms on the surface of the corroding metal and in this way the activation energy necessary for corrosion is lowered. If this is the case then such a complex should also accelerate the reverse reaction, the reduction of ferrous ion to Fe. Therefore, this hypothesis can be tested by measuring the rate of reduction of ferrous ion in the presence and absence of sulfur.

8. Steel for fatigue testing.

The Moore-Fatigue test is very costly because the specimens are expensive and a relatively large number have to be tested to obtain statistically reliable data. The main difficulty does not appear to be the test as such. It was concluded from a critical examination of the program that the steel was not uniform with respect to fatigue strength. Before resuming a Moore-Fatigue test program it is suggested that a study be made to find steel which is sufficiently uniform for testing.

9. A method for simultaneous pickling and coating.

In the pickling process the solution of the oxide film occurs and subsequently the reaction of iron with the acid. Stage 1 is desirable but stage 2 is not because the second stage is accompanied by the formation of atomic hydrogen. It is proposed that a monomer be found which can be polymerized by atomic hydrogen to form a high molecular weight insoluble substance. Thus in the pickling solution the second undesirable stage would be stopped and in addition the metal would be coated. Thus the metal can be simultaneously pickled and coated.

Identification of Technicians

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